

Synthesis and Reactivity of Silyl and Silylene Ligands in the Coordination Sphere of the 14-Electron Fragment $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}^+$

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Oxidative addition reactions of the 16-electron half-sandwich osmium complex $\text{Cp}^*(\text{iPr}_3\text{P})\text{OsBr}$ (**2**) with SiH_4 and primary and secondary hydrosilanes were examined. Compared to the previously studied ruthenium complex $\text{Cp}^*(\text{iPr}_3\text{P})\text{RuCl}$ (**1**), **2** exhibits a greater tendency to add hydrosilanes to afford stable, isolable silyl complexes. Using an abstraction–migration methodology, in which abstraction of a labile metal halide ligand is followed by 1,2-H migration from silicon to the metal center, new osmium silylene complexes were prepared. Thus, silyl complexes derived from **2** were combined with $\text{LiB}(\text{C}_6\text{F}_5)_4$ to afford cationic osmium silylene complexes of the type $[\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})_2\text{Os}=\text{SiRR}'][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{aryl, silyl}$; $\text{R}' = \text{aryl, H}$). The silylene complexes exhibit downfield ^{29}Si chemical shifts ranging from 316 ppm ($\text{R} = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$, $\text{R}' = \text{H}$; **18**) to 417 ppm ($\text{R} = \text{Si}(\text{SiMe}_3)_3$, $\text{R}' = \text{H}$; **19**). Complexes with a hydride substituent at silicon feature downfield shifts for this proton (e.g., 12.06 ppm for **19**). The reaction of $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiH}_2\text{SiPh}_3$ (**11**) with $\text{LiB}(\text{C}_6\text{F}_5)_4$ provided the unexpected rearrangement product $[\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{Ph})\text{SiPh}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**22**). Reaction of **2** with $\text{KB}(\text{C}_6\text{F}_5)_4$ produced the metalated complex $\{\text{Cp}^*[\text{iPr}_2\text{P}(\eta^2\text{-MeC}=\text{CH}_2)]\text{OsH}_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**24**), which was shown to act as a synthon for the 14-electron species $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}^+$. Thus, **24** reacted with Ph_2SiH_2 to afford $[\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})_2\text{Os}=\text{SiPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**14**).

Introduction

Many important reactions of organosilanes, such as the hydrosilylation of olefins,^{1,2} the Direct Process for the synthesis of chlorosilanes,³ and Si–H/O–H coupling,^{4,5} are promoted by transition metals. In the future, it is expected that transition metal silicon chemistry will play an even greater role in providing useful routes to silicon-based compounds and materials. Undoubtedly, this will require a better understanding of possible reaction pathways resulting from the inter-

action of organosilicon compounds with reactive transition metal centers.

A primary mode of initial silane activation by a transition metal complex involves the oxidative addition of an Si–H bond to a coordinatively unsaturated metal center to give a silyl hydride complex.⁶ Subsequent reactions of the silyl hydride complexes with additional substrates, or further rearrangements of the new silicon ligand, may provide pathways to new products. In

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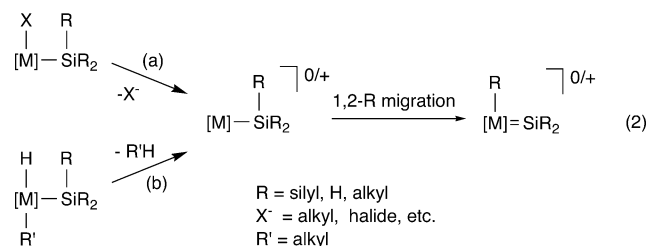
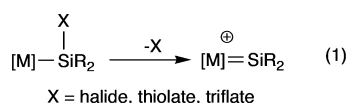
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studies on transition metal-mediated reactions of organosilanes, considerable speculation has centered on the possible role of transition metal silylene complexes in observed reactivity. Such silylene species have been proposed as intermediates in processes such as the redistribution of substituents on silicon,⁷ transfer of silylene fragments to an unsaturated carbon–carbon bond,⁸ and the Direct Process.³ Consequently, studies with isolated silylene complexes should contribute important information regarding their possible roles in observed, metal-mediated transformations.

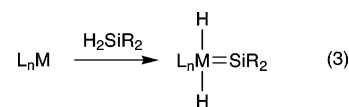
For the conversion of silyl to silylene complexes, two reaction pathways have been observed. These are anion metathesis, in which a labile substituent on silicon, such as a halide, triflate, or thiolate, is replaced with a noncoordinating anion (eq 1),⁹ and 1,2-migration of a substituent, such a hydride, silyl, or alkyl group, from silicon to an unsaturated metal center (eq 2).^{10,11}



The open coordination site required for the latter pathway may be created by abstraction of an anionic group from the metal center (path a),^{10a} reductive C–H bond elimination (path b),^{10b–e} or ligand dissociation.¹¹ For example, abstraction of the methyl ligand from the

platinum complex (κ^2 - i -Pr₂PCH₂CH₂PⁱPr₂)/Pt(Me)SiHMe₂ afforded the cationic silylene complex [(κ^2 - i -Pr₂PCH₂CH₂PⁱPr₂)(H)Pt=SiMe₂][MeB(C₆F₅)₃] via a 1,2 hydride migration from silicon to the unsaturated metal center.^{10a}

While the synthesis of silylene complexes via multi-step routes involving silyl complexes has provided important data concerning the nature of these species, synthesis of silylene complexes directly from silanes remains an important goal. Furthermore, transformations of the latter type may play a role in the development of new catalytic cycles involving silicon. In principle, the activation of two Si–H bonds at a metal center would seem to require a 14-electron metal fragment or its synthetic equivalent (eq 3). Along these lines, unsaturated iridium complexes have been employed in the conversion of secondary silanes to silylene ligands via two sequential Si–H bond activations.^{10b,c} The future development of this reactivity and its use in new catalytic pathways is likely to hinge upon the availability of a range of metal species capable of activating silanes in this manner.



Previous studies involving the coordinatively unsaturated ruthenium species Cp*(R₃P)RuCl (R = cyclohexyl, ⁱPr (1)) demonstrated that these complexes are useful precursors to a variety of electron-rich silyl and silene complexes.¹² Similarly, preliminary investigations with the related osmium complex Cp*(ⁱPr₃P)OsBr (2) demonstrated that it also oxidatively adds small molecules such as H₂ and PhSiH₃ to form stable Os(IV) species.¹³ The presence of a potentially labile bromide substituent in complexes derived from 2 suggested the use of the abstraction–migration route outlined above for the generation of new osmium silylene complexes. In particular, it seemed that the established ability of electron-rich osmium fragments to stabilize unsaturated ligands^{14–19} might facilitate the isolation of stable silylene complexes. For this reason, we have begun to explore the oxidative addition reactions of 2 with various hydrosilanes and have investigated conversions of the resulting osmium silyl derivatives to silylene complexes. Generation of a 14-electron fragment of the type Cp*(ⁱPr₃P)Os⁺, as a means to effect the direct conversion of silanes to silylene ligands (eq 3), was also targeted.

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Table 1. NMR Spectroscopic Data for Silyl Complexes 3–11

RSiH ₃	product		δ ¹ H (Si–H)	δ ²⁹ Si (Os–Si)
SiH ₄	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₃	(3)	3.59	–73.0
PhSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ Ph	(4)	6.60, 4.71	–26.0
MesSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ Mes	(5)	4.90, 4.90	–49.9
dippSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ dipp	(6)	5.05, 4.91	–53.1
tripSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ trip	(7)	4.96, 4.83	–53.0
(C ₆ F ₅)SiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ (C ₆ F ₅)	(8)	5.49, 3.98	–62.2
HexSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ Hex	(9)	5.38, 4.39	–30.5
(Me ₃ Si) ₃ SiSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ Si(SiMe ₃) ₃	(10)	5.12, 3.62	–83.5
Ph ₃ SiSiH ₃	Cp*(ⁱ Pr ₃ P)Os(H)(Br)SiH ₂ SiPh ₃	(11)	4.84, 3.19	–78.3

Results and Discussion

As described below, oxidative additions of hydrosilanes to **2** are substantially more general in scope than corresponding reactions of hydrosilanes with related ruthenium species such as Cp*(ⁱPr₃P)RuCl (**1**). While intermolecular oxidative addition reactions of hydrosilanes with **1** are limited to primary silanes such as PhSiH₃ and MesSiH₃,¹² secondary silanes such as Me₂SiH₂ and Ph₂SiH₂ add to **2** to form stable silyl complexes (vide infra). The underlying reasons for this observed difference in reactivity may include a higher metal–silicon bond strength for the osmium complexes and the greater stability of osmium(IV) versus analogous ruthenium(IV) complexes.²⁰

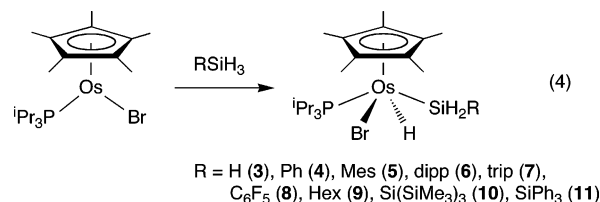
Reactions of 2 with Hydrosilanes. Despite being the simplest hydrosilane, SiH₄ has been employed in few syntheses of transition metal silyl complexes.^{6a,21} The paucity of such reports may be attributed to the difficulty in safely handling this pyrophoric reagent and to the instability of the resulting products toward further reactions.^{6a}

Exposure of a solution of **2** to an atmosphere of 15% SiH₄ in N₂ resulted in immediate formation of the bright yellow silyl complex Cp*(ⁱPr₃P)Os(H)(Br)SiH₃ (**3**), which was isolated as a yellow microcrystalline solid. When **2** was treated with excess SiH₄ in an NMR tube at room temperature, only **3** and unreacted SiH₄ were observed. The stability of the Si–H bonds in **3** to further oxidative addition may be attributed to the steric protection afforded by the Cp* and PⁱPr₃ ligands. The bimetallic complex Cp*(ⁱPr₃P)(H)(Br)Os(SiH₂)Os(Br)(H)(PⁱPr₃)Cp*, in which two osmium centers are bridged by a single silicon atom, would presumably be too sterically crowded.

A ¹H-coupled ²⁹Si INEPT NMR spectrum in which the ²⁹Si resonance appeared as a quartet of doublets of

doublets (¹J_{SiH} = 176 Hz, ²J_{SiH} = 10 Hz, ²J_{PSi} = 10 Hz) conclusively demonstrated the presence of three intact Si–H bonds in **3**. The presence of diastereotopic methyl groups on the PⁱPr₃ ligand indicated that the complex is stereochemically rigid on the NMR time scale at room temperature. The osmium-bound hydride ligand exhibits a ²J_{SiH} coupling constant of 6.2 Hz, suggesting that oxidative addition of the Si–H bond to osmium is complete in **3** and that there are no “nonclassical” interactions present.

Reactions of **2** with the primary silanes PhSiH₃, MesSiH₃, dippSiH₃ (dipp = 2,4-ⁱPr₂C₆H₃), tripSiH₃ (trip = 2,4,6-ⁱPr₃C₆H₂), (C₆F₅)SiH₃, HexSiH₃, (Me₃Si)₃SiSiH₃, and Ph₃SiSiH₃ proceeded smoothly to afford the corresponding Os(IV) silyl complexes **4**–**11** (eq 4, Table 1).



The complexes were isolated as moderately air-sensitive yellow to yellow-orange microcrystalline solids. As determined by NMR spectroscopy, yields were essentially quantitative (>95%) in all cases. The most important spectroscopic data for these complexes were obtained from ¹H and ²⁹Si NMR spectroscopy. In each case, the two silicon hydrides are rendered diastereotopic by the chiral osmium center. Each complex exhibits a single, upfield-shifted, ³¹P-coupled resonance for the osmium hydride ligand. For silyl hydride complexes of this type, the possibility exists for “nonclassical” hydrogen–silicon interactions. Species featuring such interactions, including η^2 silane complexes, often display values for ²J_{SiH} in excess of 20 Hz.^{6a,22} In the silyl complexes discussed here, coupling between the osmium hydride ligand and the silicon center, when

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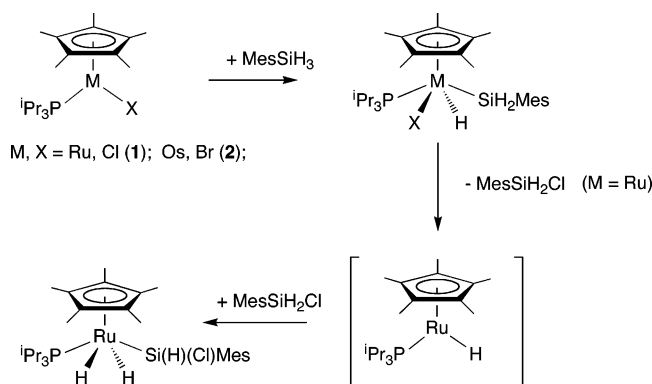
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Scheme 1



observable, was found to be below 6 Hz. For example, the value for $^2J_{\text{SiH}}$ is 5.3 Hz for **5** and is too small to be resolved in **10**.²³ These low values are inconsistent with a significant Si–H interaction.

As previously reported,^{12b} the reaction of **1** and MesSiH_3 afforded the chlorosilyl complex $\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})_2\text{RuSi}(\text{H})(\text{Cl})\text{Mes}$ instead of a dihydridosilyl complex analogous to **5**. In this reaction, it appears that the initial product $\text{Cp}^*(\text{iPr}_3\text{P})\text{Ru}(\text{H})(\text{Cl})\text{RuSiH}_2\text{Mes}$ reductively eliminates MesSiH_2Cl , which then adds to $\text{Cp}^*(\text{iPr}_3\text{P})\text{RuH}$ to afford the observed product (Scheme 1). The observed difference in reactivity between **1** and **2** may be attributed to the inherently greater lability of ruthenium complexes compared to analogous osmium species and to the greater thermodynamic driving force for the formation of a Si–Cl versus a Si–Br bond.

Reaction of $(\text{C}_6\text{F}_5)\text{SiH}_3$ with **5** (2-fold molar excess, CD_2Cl_2 solution) quantitatively afforded **8** after 7 h at room temperature. This indicates that the oxidative addition of MesSiH_3 to **2** is reversible and that **8** is thermodynamically more stable than **5**.

Reactions of secondary silanes with **1** have so far not provided isolable silyl complexes.¹² For example, in the presence of a large excess of Me_2SiH_2 , **1** was found to exist in rapid equilibrium with the corresponding oxidative addition product, precluding isolation of the product in this case.²⁴

In contrast to the behavior of **1** toward secondary silanes, **2** reacts with Me_2SiH_2 and Ph_2SiH_2 to afford $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiMe}_2\text{H}$ (**12**) and $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiPh}_2\text{H}$ (**13**), respectively, as isolable, crystalline compounds. It is reasonable to assume that greater Os–H and Os–Si bond strengths, as well as the stability of the Os(IV) oxidation state, are responsible for this pronounced difference in reactivity. The spectroscopic properties of these complexes are similar to those resulting from the oxidative additions of primary silanes. In both **12** and **13**, the two organic groups bound to silicon are diastereotopic (by NMR spectroscopy).

The steric limitations of this oxidative addition are reached with more bulky secondary silanes such as $^i\text{Pr}_2\text{SiH}_2$, Mes_2SiH_2 , and $^t\text{Bu}_2\text{SiH}_2$, which do not react

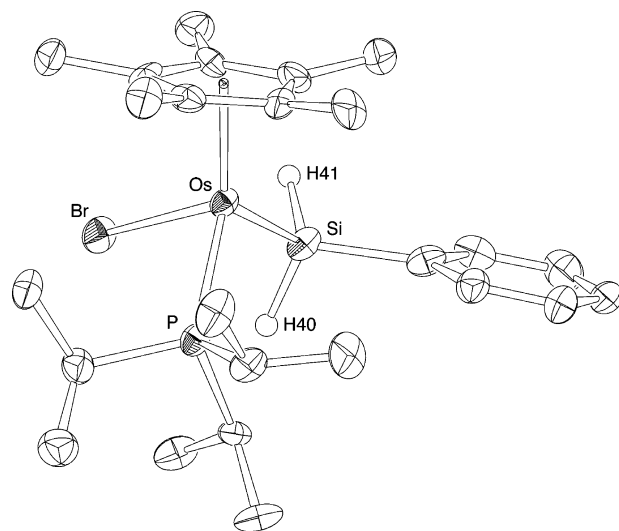


Figure 1. ORTEP drawing of **4** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) ($\text{Cp}^* = \text{C}_5\text{Me}_5$ centroid): Os–P 2.368(3), Os–Br 2.568(1), Os–Si 2.398(3), Os– Cp^* 1.9369(4), Br–Os–P 86.51(7), Br–Os–Si 79.56(7), P–Os–Si 101.0(1), Si–Os– Cp^* 120.58(8), P–Os– Cp^* 136.29(7), Br–Os– Cp^* 112.15(3).

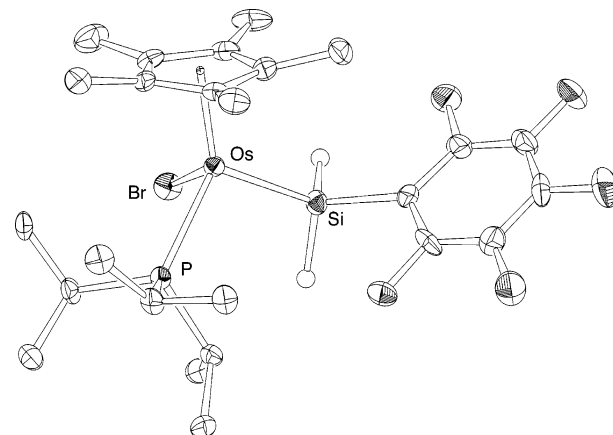


Figure 2. ORTEP drawing of **8** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) ($\text{Cp}^* = \text{C}_5\text{Me}_5$ centroid): Cp^*-Os 1.9379(1), Os–Si 2.389(2), Os–P 2.393(2), Os–Br 2.562(7), $\text{Cp}^*-\text{Os}-\text{Br}$ 112.87(2), $\text{Cp}^*-\text{Os}-\text{Si}$ 122.93(5), $\text{Cp}^*-\text{Os}-\text{P}$ 134.41(4), P–Os–Si 101.46(6), P–Os–Br 85.47(4), Br–Os–Si 76.24(5).

with **2** to afford isolable silyl complexes. Consistent with a steric explanation for this lack of reactivity, **2** was also found to be unreactive toward tertiary hydrosilanes such as Me_3SiH and Et_3SiH . Esteruelas and co-workers have previously shown that upon loss of a phosphine ligand, $\text{Cp}(\text{iPr}_3\text{P})_2\text{OsCl}$ adds Et_3SiH and Ph_3SiH , an observation consistent with the smaller steric impact of the Cp ligand versus Cp^* .²⁵

X-ray Structures of Osmium Silyl Complexes. Complexes **4**, **8**, **11**, **12**, and **13** were characterized by X-ray crystallography (Figures 1–5). In each case, the complex was found to adopt a geometry in which the

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(23) A ^{29}Si filtered ^1H NMR spectrum showed that the coupling present in this complex was on the order of the Os–H line width of 2 Hz.

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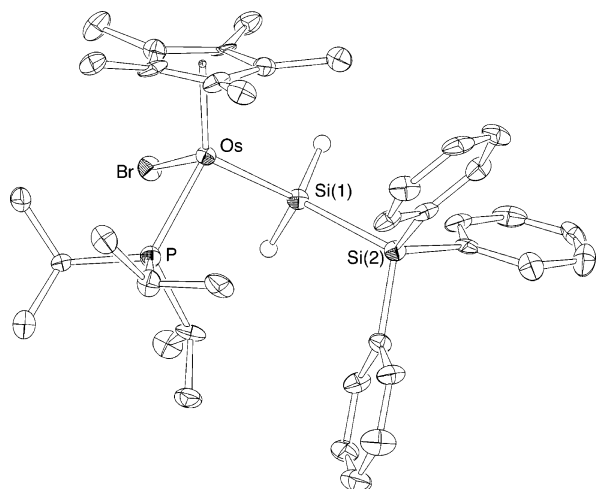


Figure 3. ORTEP drawing of **11** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) ($\text{Cp}^* = \text{C}_5\text{Me}_5$ centroid): Cp^*-Os 1.9414(3), $\text{Os}-\text{Si}(1)$ 2.406(3), $\text{Os}-\text{P}$ 2.382(3), $\text{Os}-\text{Br}$ 2.567(1), $\text{Si}(1)-\text{Si}(2)$ 2.378(4), $\text{Cp}^*-\text{Os}-\text{Si}$ 110.26(3), $\text{Cp}^*-\text{Os}-\text{Br}$ 112.19(7), $\text{Cp}^*-\text{Os}-\text{P}$ 136.43(7), $\text{Os}-\text{Si}(1)-\text{Si}(2)$ 126.1(1), $\text{P}-\text{Os}-\text{Si}$ 100.00(9), $\text{P}-\text{Os}-\text{Br}$ 85.60(7), $\text{Br}-\text{Os}-\text{Si}$ 80.01(7).

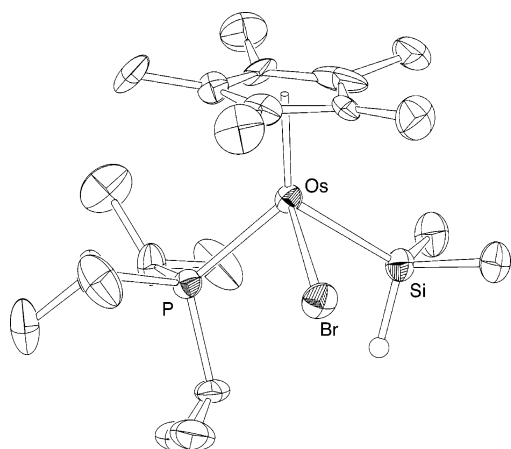


Figure 4. ORTEP drawing of **12** with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) ($\text{Cp}^* = \text{C}_5\text{Me}_5$ centroid): Cp^*-Os 1.9471(8), $\text{Os}-\text{Si}$ 2.431(6), $\text{Os}-\text{P}$ 2.379(5), $\text{Os}-\text{Br}$ 2.574(2), $\text{Cp}^*-\text{Os}-\text{Si}$ 115.15(6), $\text{Cp}^*-\text{Os}-\text{Br}$ 126.7(1), $\text{Cp}^*-\text{Os}-\text{P}$ 130.6(1), $\text{P}-\text{Os}-\text{Si}$ 99.8(2), $\text{P}-\text{Os}-\text{Br}$ 87.1(1), $\text{Br}-\text{Os}-\text{Si}$ 78.6(2).

phosphine, hydride, bromide, and silyl substituents form the “legs” of a “four-legged piano stool”, in which the triisopropylphosphine and the silyl substituents are in mutually *transoid* positions.²⁶ Whereas the silyl groups derived from primary silanes and small secondary silanes can adopt a conformation in which steric interactions with the Cp^* and P^iPr_3 ligands are minimized, this is not possible for large secondary or tertiary silyl groups.

The bond lengths and angles for this series of complexes are all relatively similar (Table 2). The $\text{Os}-\text{Si}$ bond lengths range from 2.389(2) Å in **8** to 2.431(6) Å in **12**.

(26) The position of the osmium hydride ligand in these complexes could not be reliably located by X-ray crystallography and is inferred from the positions of the other ligands on osmium and by spectroscopic measurements.

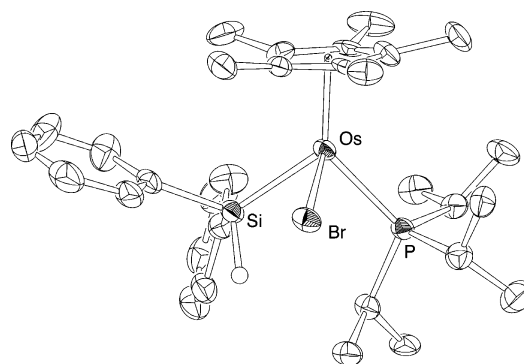


Figure 5. ORTEP drawing of one of the two similar molecules of **13** in the asymmetric unit with thermal ellipsoids at the 50% probability level. Non-silicon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) ($\text{Cp}^* = \text{C}_5\text{Me}_5$ centroid): Cp^*-Os 1.9409(3), $\text{Os}-\text{Si}$ 2.414(2), $\text{Os}-\text{P}$ 2.382(2), $\text{Os}-\text{Br}$ 2.5655(8), $\text{Cp}^*-\text{Os}-\text{Si}$ 111.63(2), $\text{Cp}^*-\text{Os}-\text{Br}$ 127.21(5), $\text{Cp}^*-\text{Os}-\text{P}$ 135.56(5), $\text{P}-\text{Os}-\text{Si}$ 94.78(7), $\text{P}-\text{Os}-\text{Br}$ 85.83(5), $\text{Br}-\text{Os}-\text{Si}$ 81.25(5).

Osmium Silylene Complexes via 1,2-Hydrogen Migrations. It was reasoned that abstraction of the bromide substituent of an osmium silyl species might promote a hydride migration process and allow access to cationic osmium silylene complexes (Scheme 2).

Treatment of **13** with the anion metathesis reagent $\text{LiB}(\text{C}_6\text{F}_5)_4 \cdot 3\text{Et}_2\text{O}$ in CD_2Cl_2 afforded a product having C_s symmetry (on the NMR time scale) and formulated as the osmium dihydride silylene complex $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{OsSiPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]$, as determined by ^1H and ^{13}C NMR spectroscopy. A ^{29}Si resonance could not be detected for this species (23 °C, CD_2Cl_2 solution), possibly because of a dynamic interaction with Et_2O or LiBr in solution. Such a process could dramatically broaden the ^{29}Si resonance of the silylene complex. Unfortunately, attempts to separate the organometallic product from LiBr and Et_2O by crystallization or precipitation were unsuccessful and resulted in either the recovery of starting material or decomposition (apparently, small amounts of Et_2O efficiently solubilize LiBr in CH_2Cl_2 and fluorobenzene). Removal of volatile materials from reaction mixtures containing Et_2O under high vacuum and subsequent workup afforded only impure products that retained Et_2O . This behavior contrasts with that of the previously described bis-phosphine silylene complexes $[\text{Cp}^*(\text{Me}_3\text{P})_2\text{MSiR}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{M} = \text{Ru}, \text{Os}$), which can be recrystallized as base-free complexes from solutions containing ethereal solvents.^{9h-j,l,m}

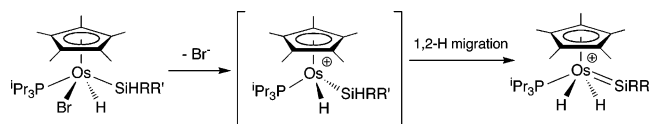
Use of the ether-free borate reagent $\text{LiB}(\text{C}_6\text{F}_5)_4$ facilitated preparation of the pure silylene complex $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{SiPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**14**). In the absence of Et_2O , LiBr precipitates from CH_2Cl_2 solution and can be removed by filtration. The resulting complex has effective C_s symmetry on the NMR time scale and exhibits a single set of resonances for the triisopropylphosphine methyl groups, one upfield resonance integrating to two protons for two mutually *transoid* osmium hydrides, and a sharp, ^{31}P -coupled ^{29}Si resonance at 313 ppm. The observed value for $^2J_{\text{SiH}}$ (5.5 Hz) is inconsistent with a significant silicon–hydrogen interaction in **14**.

Exhaustive attempts to crystallize **14** and the other osmium silylene complexes described below were unsuccessful.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Crystallographically Characterized Osmium Silyl Complexes Derived from **1**

	4	8	11	12	13 ^b	15
Cp*–Os ^a	1.9369(4)	1.9378(1)	1.9414(3)	1.9471(8)	1.9409(3)	1.9534(3)
Os–Si	2.398(3)	2.389(2)	2.406(3)	2.431(6)	2.414(2)	2.355(2)
Os–P	2.368(3)	2.393(2)	2.382(3)	2.379(5)	2.382(2)	2.358(2)
Os–Br	2.568(1)	2.5627(7)	2.567(1)	2.574(2)	2.5655(8)	2.5723(8)
Cp*–Os–Br	112.15(3)	112.87(2)	110.26(3)	115.15(6)	111.63(2)	111.45(2)
Cp*–Os–Si	120.58(8)	122.93(5)	112.19(7)	126.7(1)	127.21(5)	127.92(5)
Cp*–Os–P	136.29(7)	134.41(4)	136.43(7)	130.6(1)	135.56(5)	134.76(5)
P–Os–Si	101.0(1)	101.46(6)	100.00(9)	99.8(2)	94.78(7)	94.98(7)
P–Os–Br	86.51(7)	85.47(4)	85.60(7)	87.1(1)	85.83(5)	86.34(5)
Br–Os–Si	79.56(7)	76.24(5)	80.01(7)	78.6(2)	81.25(5)	80.71(6)
Os–Si–C	120.3(3)	118.3(2)	126.1(1) ^c	116.6(7)	118.1(3)	118.7(3)
				117.7(8)	116.7(3)	116.7(3)
C–Si–C				103(1)	104.4(4)	103.2(4)
						105.2(3)

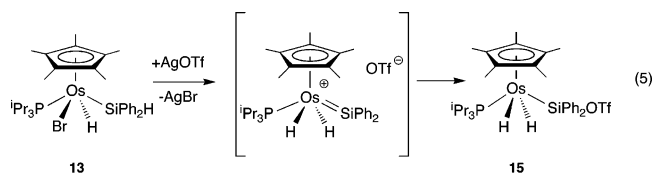
^a Cp* = C₅Me₅ centroid. ^b Two crystallographically independent molecules in the unit cell. ^c Os–Si–Si.

Scheme 2

cessful. Cooling concentrated CH₂Cl₂ or C₆H₅F solutions failed to afford solid products, and various hydrocarbon–halocarbon and fluoroether–halocarbon solvent mixtures led primarily to phase separation and precipitation of the products as viscous orange oils. Difficulties in crystallizing ionic species containing large, very weakly coordinating anions such as B(C₆F₅)₄⁻ are often attributed to the low lattice energies of such substances.²⁷ Attempts to increase the crystallinity of the silylene complexes by employing the {B[3,5-(CF₃)₂C₆H₃]₄}⁻ anion were unsuccessful and led to decomposition. This anion is known to be more susceptible than B(C₆F₅)₄⁻ to electrophilic attack by a Lewis acidic silicon species.²⁸

Removal of solvent from solutions of the silylene complexes described here, including **14**, afforded dark yellow oils which solidified as foams after prolonged exposure to vacuum. These foams tenaciously retained small quantities of solvent, making combustion analyses unreliable. The silylene complexes decomposed over the course of days in the solid state to afford complicated mixtures of products. For these reasons, the silylene complexes (other than **18**) were characterized in solution using multinuclear NMR spectroscopy.

The reaction of **13** with AgOTf gave the silyltriflate complex Cp*(iPr₃P)(H)₂OsSiPh₂OTf (**15**; eq 5).



In contrast to the silylene complex [Cp*(Me₃P)(H)-IrSiMes₂][OTf],^{9j} the triflate group in **15** remains coor-

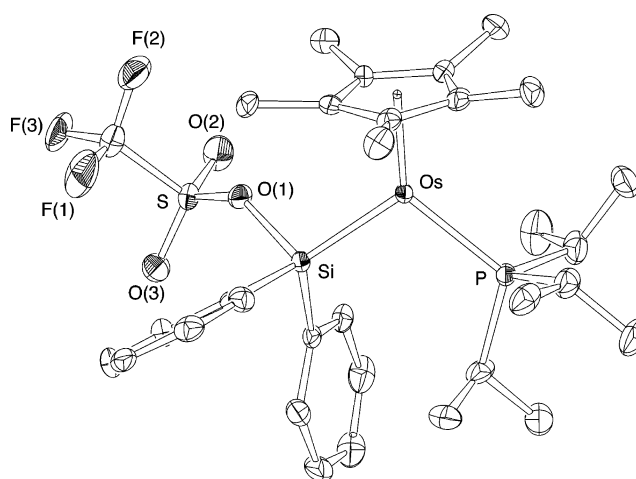


Figure 6. ORTEP drawing of **15** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C₅Me₅ centroid): Cp*–Os 1.9348(3), Os–Si 2.355(2), Os–P 2.358(2), Si–O(1) 1.847(5), Cp*–Os–Si 123.98(5), Cp*–Os–P 131.72(4), P–Os–Si 104.24(6), Os–Si–O(1) 107.6(2).

minated to the silicon center both in CD₂Cl₂ solution, as determined by NMR spectroscopy, and in the solid state, as determined by X-ray crystallography (Figure 6). The Os–Si bond in **15** is significantly shorter than the corresponding bond in **13** (Table 2), and the sum of the Os–Si–C and the C–Si–C bond angles in **15** is 346.3° (for comparison, this sum is 339.2° for **13**). These observations are consistent with a greater amount of silylene character at the silicon center of **15**.

Silylene Complexes of the Type [Cp*(iPr₃P)-(H)₂Os=Si(H)R]⁺. Silylene complexes derived from dihydrosilyl derivatives, L_nM–SiH₂R, are of particular interest, as silylene complexes possessing an Si–H bond represent a very rare structure type with relatively unexplored reactivity and spectroscopic properties.^{10b,29}

In an attempt to synthesize a cationic silylene complex of the type [L_nM=SiH₂]⁺, **3** was treated with LiB(C₆F₅)₄ in CD₂Cl₂. This reaction afforded a single major product that featured resonances in the ¹H NMR spectrum consistent with a highly fluxional structure.

(27) (a) Bond, D. R.; Jackson, G. E.; Joao, H. C.; Hofmeyer, M. N.; Modro, T. A.; Nassimbein, L. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1910. (b) Hunter, R.; Haueisan, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 566. (c) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, 15, 3859. (d) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, 121, 5001.

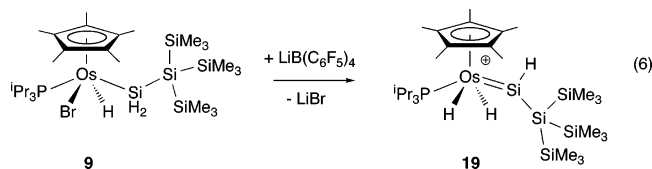
(28) (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, 114, 6697. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, 31, 325.

(29) (a) Simons, R. S.; Gallucci, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2002**, 654, 224. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, 43, 218. (c) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, 126, 10428.

In the ^1H NMR spectrum, the Cp^* and P^iPr_3 peaks of the product are sharp, but the resonances associated with the presumed SiH_2 silylene group ($\delta(^1\text{H}) = 6.2$ ppm) and the metal-bound hydride ($\delta(^1\text{H}) = -14.8$ ppm) were broad and featureless. A ^{29}Si resonance could not be detected for this species. The identities of the species in solution are unclear, but low-temperature NMR data are consistent with reversible aggregation to a low-symmetry complex tentatively formulated as $\{[\text{Cp}^*(^i\text{Pr}_3\text{P})\text{Os}(\text{H})_2\text{Os}=\text{SiH}_2][\text{B}(\text{C}_6\text{F}_5)_4]\}_n$ (**16**).

Various reactions of $\text{LiB}(\text{C}_6\text{F}_5)_4$ with $\text{Cp}^*(^i\text{Pr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiH}_2\text{R}$ did not cleanly generate silylene complexes when $\text{R} = \text{Ph}$ (**4**), Mes (**5**), or Hex (**9**). However, reaction of $\text{LiB}(\text{C}_6\text{F}_5)_4$ with silyl complexes possessing more sterically demanding substituents on silicon afforded cationic osmium silylene species of the type $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{H})\text{R}][\text{B}(\text{C}_6\text{F}_5)_4]$. These silylene complexes are distinguished by C_s symmetry on the NMR time scale and downfield ^{29}Si and ^1H shifts for the silylene center and the silicon-bound proton, respectively. For example, for $\text{R} = \text{trip}$ (**17**), the $\text{Si}-\text{H}$ resonance appears at 11.56, and $\delta(^{29}\text{Si}) = 315$ ppm. These values parallel the downfield ^{13}C and ^1H chemical shifts observed in metal carbene complexes of the type $\text{M}=\text{C}(\text{H})\text{R}^{30}$ and reflect sp^2 hybridization at silicon. As demonstrated by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, the large aryl groups in **16** ($\text{R} = \text{dipp}$) and **17** rotate freely about their $\text{Si}-\text{C}$ bonds, rendering the *ortho*-isopropyl methyl groups equivalent on the NMR time scale.

The silylene complex derived from **9**, $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{H})\text{Si}(\text{SiMe}_3)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**19**; eq 6),



exhibits a downfield ^1H chemical shift for the $\text{Si}-\text{H}$ group at 12.05 ppm and a very downfield-shifted ^{29}Si resonance at 417.5 ppm. Surprisingly, the $^1J_{\text{SiH}}$ coupling constant for **19** is 147 Hz, a value approximately 30 Hz lower than the $^1J_{\text{SiH}}$ values in **9**. The steric demands of the $\text{Si}(\text{SiMe}_3)_3$ group bound to silicon should favor a large $\text{Os}-\text{Si}-\text{Si}$ angle in **19**, which would, in turn, decrease the amount of s -character in the $\text{Si}-\text{H}$ bond, causing a decreased value for $^1J_{\text{SiH}}$. For comparison, the values for $^1J_{\text{SiH}}$ in **17** (188 Hz) and **18** (184 Hz) are essentially identical to those in the corresponding silyl complexes. It is interesting to note that the β -silicon atom in **19** has a ^{29}Si chemical shift of -74.9 ppm. Consequently, ^{29}Si chemical shifts spanning nearly 500 ppm are found in a single molecule.

Reaction of **8** with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in CD_2Cl_2 afforded $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{H})(\text{C}_6\text{F}_5)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**20**), as determined by NMR spectroscopy. While the ^{29}Si resonance of **20** appears at 318 ppm, the silicon-bound hydride appears at only 6.75 ppm. The origin of the disparity between the chemical shifts of the $\text{Si}-\text{H}$ resonances in **17**–**19** and that of **20** is not entirely clear. The ^{29}Si chemical shift of **20** is inconsistent with a four-coordinate silicon center that might result from intramolecular donation by an aryl $\text{C}-\text{F}$ group to the silylene silicon center. The ^{19}F NMR spectrum of **20** exhibits

three resonances for the cation in **20**, but the *ortho*- F resonances are significantly broader than the *meta* and *para* resonances. Fluorocarbons are known to be exceedingly poor hydrogen bond acceptors,³¹ but the close proximity of the C_6F_5 group to the silicon-bound hydrogen, the relatively organized structure of **20**, and the inductive effect of the electrophilic silylene center on the $\text{Si}-\text{H}$ bond could favor an unusual interaction between an *ortho*-fluorine and the silicon-bound hydrogen in **20**.

Treatment of $\text{Cp}^*(^i\text{Pr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiH}_2\text{SiPh}_3$ (**11**) with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in CD_2Cl_2 afforded a single product displaying two equivalent osmium hydride resonances and a single $\text{Si}-\text{H}$ resonance having a chemical shift of 5.78 ppm, a value that would seem to be inconsistent with an $\text{Os}=\text{Si}(\text{H})\text{R}^+$ structure. Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum indicates that the SiPh_3 group of the starting material is not intact in the presumed silylene product. A $^{29}\text{Si}-^1\text{H}$ HMQC NMR experiment demonstrated that the hydrogen resonating at 5.78 ppm is bound to the β -silicon in the product, instead of the metal-bound silicon. It was therefore concluded that a nascent silylene complex formulated as $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{H})(\text{SiPh}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**21**) undergoes an isomerization involving the exchange of a phenyl group with the silylene hydrogen to afford $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{Ph})(\text{SiPh}_2\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**22**). Related 1,2-migrations between silicon and electrophilic centers have been previously observed and studied with theoretical methods.³² Reaction of **11** with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in the presence of the strongly coordinating base 4-(dimethylamino)pyridine (DMAP) afforded a single product that contained an intact SiPh_3 group and a single $\text{Si}-\text{H}$ bond, as determined by multinuclear NMR spectroscopy. This new product was formulated as the "intercepted" silylene complex $[\text{Cp}^*(^i\text{Pr}_3\text{P})(\text{H})_2\text{Os}=\text{Si}(\text{H})(\text{SiPh}_3)(\text{DMAP})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**21**·DMAP) (Scheme 3). This product is not formed upon reaction of **22** with DMAP.

Upon monitoring the reaction of **11** with $\text{LiB}(\text{C}_6\text{F}_5)_4$ in CD_2Cl_2 at low temperature by NMR spectroscopy, an intermediate (**23**) was observed. This intermediate reached a maximum concentration of approximately 70% after 2 min at 0 $^\circ\text{C}$. Thereafter, the intensities of the resonances associated with this species rapidly decreased as the concentration of **22** increased. The intermediate exhibited two inequivalent osmium hydride resonances ($\delta(^1\text{H}) = -13.97$ and -14.37 ppm) and a single broad $\text{Si}-\text{H}$ peak at 5.98 ppm in its ^1H NMR spectrum. The observation of two inequivalent hydride ligands in **23** suggests the presence of a chiral silicon center bound to osmium. Thus, the conversion of **21** to **22** appears to proceed by the 1,2-migration of a phenyl group from the β -silicon atom of **21** its silylene center to generate **23**. A 1,2 hydrogen migration would then complete the formation of **22** (Scheme 3).

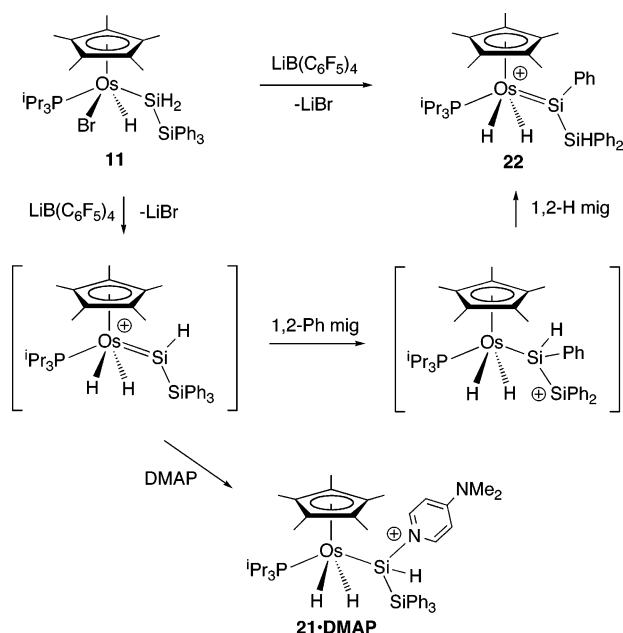
A Metalated Triisopropylphosphine Complex as a Formal Synthon for the 14-Electron Cation

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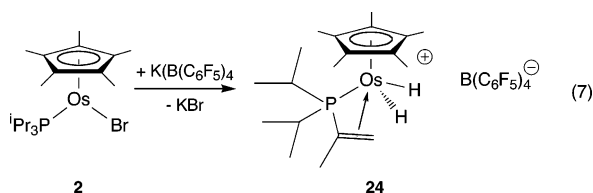
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Scheme 3



Cp*(iPr₃P)Os⁺. As demonstrated by the studies described above, coordinatively unsaturated osmium complexes are potentially very useful in the synthesis of silylene complexes. From the 16-electron complex **2**, silylene complexes are obtained in two steps involving oxidative addition of a silane followed by a bromide abstraction. In principle, the formally 14-electron complex Cp*(iPr₃P)Os⁺ could serve as a more direct precursor to cationic [Cp*(iPr₃P)(H)₂Os=SiRR']⁺ silylene complexes via the double Si–H bond activation of a hydrosilane (eq 3). To investigate a possible route to Cp*(iPr₃P)Os⁺ (or a synthon thereof), the metathesis of the bromide in **2** with the noncoordinating B(C₆F₅)₄[−] anion was attempted.

Reaction of **2** with 1 equiv of KB(C₆F₅)₄ in THF/CH₂Cl₂ afforded the unexpected cationic species {Cp*[iPr₂P(η²-MeC=CH₂)]OsH₂}[B(C₆F₅)₄] (**24**; eq 7).



Presumably, exchange of the bromide substituent with the noncoordinating B(C₆F₅)₄[−] anion affords a transient, formally 14-electron intermediate Cp*(iPr₃P)Os⁺, which then activates two of the C–H bonds in the triisopropylphosphine ligand (Scheme 4).³³ The solid-state structure of **24** is shown in Figure 7. The metalated isopropyl group is planar within error, indicating sp² hybridization of the phosphorus-bound carbon atom. Recently

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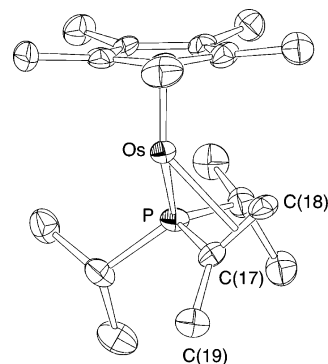
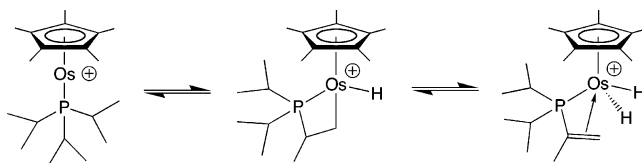


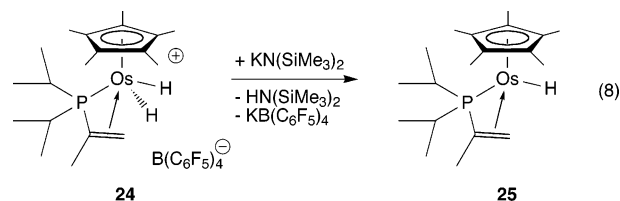
Figure 7. ORTEP drawing of **24** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the B(C₆F₅)₄[−] counterion are omitted for clarity. Selected bond lengths (Å) and angles (deg) (Cp* = C₅Me₅ centroid, CC = midpoint of C(17) and C(18)): Os–P 2.320(2), Os–Cp* 1.8958(3), Os–CC 2.0680(3), C(17)–C(18) 1.43(1), C(17)–C(19) 1.49(1), Cp*–Os–P 134.02(5), Cp*–Os–CC 136.59(2), P–Os–CC 67.09(5), P–C(17)–C(18) 109.9(5), P–C(17)–C(19) 126.0(6), C(18)–C(17)–C(19) 124.1(7).

Scheme 4



reported examples of metalated triisopropylphosphine ligands have also been described as chelating α-alkenylphosphine ligands. The ¹H NMR spectrum of **24** is consistent with its solid-state structure and features two distinct osmium hydride resonances and five intact and magnetically inequivalent isopropyl methyl groups.

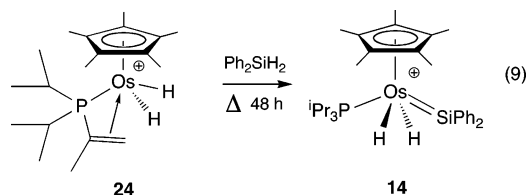
Complex **24** was deprotonated with KN(SiMe₃)₂ to afford the neutral, hydrocarbon-soluble species Cp*[iPr₂P(η²-MeC=CH₂)]OsH (**25**; eq 8).



This reaction is conveniently carried out in benzene, a solvent in which **24** forms a dense, insoluble oil and KB(C₆F₅)₄ is insoluble. Complex **25** is a viscous oil that is exceedingly soluble in common solvents such as hydrocarbons and Et₂O, and for this reason, it could not be crystallized. Thus, this compound was only characterized by multinuclear NMR spectroscopy.

Although complexes **24** and **25** are both coordinatively saturated 18-electron complexes, it was thought that they might function as synthons for 14-electron Cp*(iPr₃P)Os⁺ via reductive elimination processes (Scheme 4). In fact, the reaction of **24** with Ph₂SiH₂ in CD₂Cl₂ at 80 °C in a sealed NMR tube for 48 h afforded the diphenylsilylene complex **14** as the major component of a mixture of products, as determined by NMR spectroscopy (eq 9). Although the generation of **14** from **24** is a demonstration of double Si–H activation by a

$\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}^+$ surrogate, the synthesis of **14** is accomplished more rapidly and with fewer byproducts from the reaction of the isolable silyl complex **13** with $\text{LiB}(\text{C}_6\text{F}_5)_4$.



Concluding Remarks

The 16-electron complex **2** is a useful starting precursor to a series of stable osmium silyl complexes derived from hydrosilanes. Compared to the similar ruthenium complex **1**, **2** reacts with a wider variety of silanes, including secondary silanes such as Ph_2SiH_2 and Me_2SiH_2 . This enhanced reactivity is attributed to the greater strength of bonds to osmium and the stability of $\text{Os}(\text{IV})$ versus $\text{Ru}(\text{IV})$ in analogous complexes.

The successful reactions of $\text{LiB}(\text{C}_6\text{F}_5)_4$ with these silyl complexes to afford silylene complexes under relatively mild conditions are examples of the utility of the abstraction–migration route to silylene complexes. Since the silyl complexes used in this method are derived from relatively simple hydrosilanes, the abstraction–migration route for the synthesis of silylene complexes may have greater versatility than previously employed routes to silylenes that require more complex silicon starting materials, such as alkylchlorohydridosilanes or thiolatosilanes. The successful preparation of a series of complexes featuring the $\text{M}=\text{Si}(\text{H})\text{R}$ structural motif should provide greater insight into the reactivity modes of this class of silylene complexes.

Attempted generation of the 14-electron complex $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}^+$ via reaction of $\text{KB}(\text{C}_6\text{F}_5)_4$ with **2** instead afforded the 18-electron complex $\{\text{Cp}^*[\text{iPr}_2\text{P}(\eta^2\text{-MeC}=\text{CH}_2)]\text{OsH}_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$. This complex features an unusual orthometalated alkylphosphine ligand resulting from the double C–H activation of an isopropyl group. The complex was shown to slowly react with Ph_2SiH_2 to afford the diphenylsilylene complex **14**, demonstrating the ability of a 14-electron synthon to convert hydrosilanes directly to silylene ligands through double Si–H activation. Improved understanding of the conversion of hydrosilanes to silylenes may contribute to the understanding of previously observed reactions believed to operate through mechanisms including silylene intermediates.

We are currently exploring the potential utility of cationic silylene complexes of the type $\text{L}_n\text{M}=\text{Si}(\text{H})\text{R}^+$ for use as catalysts in a variety of organic transformations. Initial results have shown that such silylene complexes catalyze the selective hydrosilylation of alkenes by an unexpected mechanism.³⁴ It is hoped that new systems can be identified in which double Si–H activation processes are rapid enough for incorporation into useful catalytic cycles.

Experimental Section

Manipulations involving air-sensitive compounds were conducted using standard Schlenk techniques under a purified

N_2 atmosphere or in a Braun Uni-Lab drybox. Nondeuterated solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents, vacuum-transferred before use, and stored over molecular sieves.

Previously described methods were used to prepare $\text{Cp}^*(\text{iPr}_3\text{P})\text{OsBr}$,¹³ $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]\cdot 3\text{Et}_2\text{O}$,³⁵ $\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{-(SiH}_2\text{Ph)}$,¹³ $(\text{C}_6\text{F}_5)_3\text{SiH}_3$,³⁶ and $\text{KN}(\text{SiMe}_3)_2$.³⁷ Both $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ were generous gifts of Boulder Scientific Co. The silanes $(\text{Me}_3\text{Si})_3\text{SiSiH}_3$, $\text{Ph}_3\text{SiSiH}_3$, PhSiH_3 , dippSiH_3 , and tripSiH_3 were prepared by the LiAlH_4 reduction of the corresponding silyl chlorides.³⁸ Liquid silanes were fractionally distilled under N_2 and stored over molecular sieves. Solid silanes were recrystallized from Et_2O and dried in vacuo. Hexylsilane and Ph_2SiH_2 were purchased from Gelest Co., degassed, and stored over molecular sieves. Dimethylsilane and 15% SiH_4 in N_2 were purchased from Gelest Co. and used as received.

NMR spectra were acquired on a Bruker DRX-500 spectrometer equipped with a 5 mm BBI probe or a Bruker AVB-400 spectrometer equipped with a 5 mm gradient BB probe. Spectra were recorded at room temperature and were referenced to protio-impurities in the deuterated solvent for ^1H , solvent peaks for ^{13}C , CFCl_3 for ^{19}F , SiMe_4 for ^{29}Si , and 85% H_3PO_4 for ^{31}P . Multiplets that appear as virtual triplets or quartets are denoted as “vt” or “vq”, respectively. Resonances assignable to the $\text{B}(\text{C}_6\text{F}_5)_4$ anion are not reported. When necessary, DEPT and ^1H – ^{13}C gHMQC detection schemes were employed in the assignment of ^{13}C and ^1H resonances. The gHMBC experiment used for ^{29}Si detection has a nominal resolution of approximately 1 ppm under standard conditions. Combustion analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

$\text{Cp}^*(\text{iPr}_3\text{P})\text{Os}(\text{H})(\text{Br})\text{SiH}_3$ (3**).** WARNING: At concentrations of 15% in N_2 , SiH_4 is pyrophoric and should only be handled by qualified individuals with adequate safety precautions in place. A heavy-walled 100 mL reaction vessel equipped with an 8 mm PTFE valve and a 24/40 ground glass joint was charged 312 mg of **2** and a small magnetic stirbar. The solid was dissolved in approximately 15 mL of Et_2O to afford a purple solution. The vessel was attached directly to a Schlenk line, and the solution was degassed through a series of freeze–pump–thaw cycles. The vessel was then cooled to -78°C and charged with 1 atm of SiH_4 (15% in N_2). The color of the vigorously stirred solution rapidly changed from purple to orange. The cooling bath was removed, and the solution was allowed to warm to room temperature. Stirring was continued until the solution had become a uniform banana-yellow color and a fine yellow precipitate had formed. Unreacted SiH_4 was then vented to the atmosphere with a N_2 cross-purge and allowed to inflame. The solution was stirred under an atmosphere of N_2 for an additional 10 min, and solvent was then removed in vacuo. The powdery yellow residue was extracted with two 5 mL portions of 3:1 $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$. The combined filtrates were cooled slowly to -80°C over 16 h to afford well-formed orange-yellow crystals (192 mg). Removing the solvents from the filtrates afforded an additional 61 mg of analytically pure **3** as a fine yellow powder. Yield: 253 mg (76%). ^1H NMR (CD_2Cl_2 , δ): 3.59 (s, 3 H, $J_{\text{SiH}} = 174.6$ Hz, OsSiH_3), 2.51 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 1.74 (d, 15 H, $J_{\text{PH}} = 1.5$ Hz, C_5Me_5), 1.12–

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1.20 (2 overlapping vq, 18 H, P(CHMe₂)₃), -15.35 (d, 1 H, ²J_{PH} = 32 Hz, OsH). ¹³C{¹H} NMR (CD₂Cl₂, δ): 94.11 (d, J_{PH} = 2 Hz, C₅Me₅), 28.03 (d, ²J_{PH} = 27.1, P(CHMeMe)₃), 20.28, 19.86 (P(CHMe₂)₃), 10.19 (C₅Me₅). ³¹P{¹H} NMR (CD₂Cl₂, δ): 12.19. ²⁹Si NMR (coupled INEPT, δ): -72.97 (qdd, ¹J_{SiH} = 176 Hz, ²J_{SiH} = 10 Hz, ²J_{PSi} = 10 Hz). Anal. Calcd: C, 38.18; H, 6.75. Found: C, 38.51; H, 6.98.

Cp*(Pr₃P)Os(H)(Br)SiH₂Mes (5). To a stirred solution of 500 mg (0.881 mmol) of **2** in approximately 25 mL of Et₂O was added slowly by cannula at room temperature 145 mg (0.97 mmol) of MesSiH₃ in 10 mL of Et₂O. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 15 mL and slowly cooled to -80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration and dried in vacuo. Yield: 475 mg (75%). ¹H NMR (CD₂Cl₂, δ): 6.78 (s, 2 H, aryl), 4.9 (br s, 2 H, ¹J_{SiH} = 176 Hz, SiH₂Mes), 2.68 (s, 3 H, 4-Me), 2.52 (s, 6 H, 2,6-Me), 2.44 (m, 3 H, P(CHMe₂)₃), 1.63 (s, 15 H, C₅Me₅), 1.11–1.16 (vq, 9 H, P(CHMeMe)₃), 1.07–1.11 (vq, 9 H, P(CHMeMe)₃), -15.04 (d, 1 H, ²J_{PH} = 29.4 Hz, OsH). ¹³C{¹H} NMR (CD₂Cl₂, δ): 144.5, 136.8, 136.5, 127.5 (aryl), 94.2 (C₅Me₅), 28.2 (d, ¹J_{CP} = 25.8 Hz, P(CHMe₂)₃), 23.9, 20.7 (C₆H₂Me₃), 19.8 (d, ²J_{CP} = 3.1 Hz, P(CHMeMe)₃), 19.7 (P(CHMeMe)₃), 10.2 (C₅Me₅). ³¹P{¹H} NMR (CD₂Cl₂, δ): 3.9. ²⁹Si{¹H} NMR (CD₂Cl₂, HMBC, δ): -49.9 (d, ²J_{SiP} = 9.8 Hz). Anal. Calcd for C₂₈H₅₀BrOsPSi: C, 46.98; H, 7.04. Found: C, 47.29; H, 7.24.

Cp*(Pr₃P)Os(H)(Br)SiH₂dipp (6). To a stirred solution of 175 mg (308 mmol) of **2** in approximately 25 mL of pentane was added slowly by cannula at room temperature 61 mg (0.32 mmol) of dippSiH₃ in 10 mL of pentane. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 10 mL and slowly cooled to -80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration, washed with two 10 mL portions of pentane at -78 °C, and dried in vacuo. Yield: 131 mg (56%). ¹H NMR (CD₂Cl₂, δ): 7.20 (t, 1 H, ³J_{HH} = 8 Hz, *p*-aryl), 7.09 (d, 2 H, ³J_{HH} = 8 Hz, *m*-aryl), 5.05 (d, 1 H, ²J_{HH} = 4.8 Hz, ¹J_{SiH} = 178 Hz, SiHH), 4.91 (d, 1 H, ²J_{HH} = 4.8 Hz, ¹J_{SiH} = 181 Hz, SiHH), 3.73 (sept, 2 H, ³J_{HH} = 7 Hz, *m*-CHMe₂), 2.52 (m, 3 H, P(CHMe₂)₃), 1.68 (s, 15 H, C₅Me₅), 1.26 (d, 12 H, 7 Hz, *m*-CHMe₂), 1.21 (vq, 9 H, P(CHMeMe)₃), 1.09 (vq, 9 H, P(CHMeMe)₃), -15.00 (d, 1 H, ²J_{PH} = 29.3 Hz, Os-H). ¹³C{¹H} NMR (CD₂Cl₂, δ): 156.1 (*m*-aryl), 138.1, (ipso-aryl), 128.5, 122.0 (aryl), 94.6 (C₅Me₅), 33.4 (*o*-CHMe₂), 28.7 (d, ¹J_{PC} = 27 Hz, P(CHMe₂)₃), 25.3, 24.8 (*o*-CHMe₂), 20.2, 20.0 (P(CHMe₂)₃), 10.8 (C₅Me₅). ²⁹Si{¹H} NMR (CD₂Cl₂, δ): -53.1. ³¹P{¹H} NMR (CD₂Cl₂, δ): 4.31. Anal. Calcd for C₃₁H₅₆BrOsPSi: C, 49.12; H, 7.45. Found: C, 49.33; H, 7.65.

Cp*(Pr₃P)Os(Br)(H)SiH₂trip (7). To a stirred solution of 600 mg (1.06 mmol) of **1** in approximately 25 mL of pentane was added slowly by cannula at room temperature 367 mg (1.48 mmol) of tripSiH₃ in 10 mL of pentane. The mixture's color quickly turned from purple to golden yellow-orange. The solution was concentrated in vacuo to approximately 10 mL and slowly cooled to -80 °C. After 1 day, a microcrystalline precipitate had formed. The product was isolated by filtration, washed with two 10 mL portions of pentane at -78 °C, and dried in vacuo. Yield: 715 mg (85.1%). ¹H NMR (CD₂Cl₂, δ): 6.92 (s, 2 H, aryl H), 4.96 (d, 1 H, ²J_{HH} = 4 Hz, ¹J_{SiH} = 178 Hz, Os-SiH), 4.83 (d, 1 H, ²J_{HH} = 4 Hz, ¹J_{SiH} = 179 Hz, Os-SiH), 3.70 (sept, 2 H, ³J_{HH} = 7 Hz, CHMe₂), 2.82 (sept, 1 H, ³J_{HH} = 7 Hz, CHMe₂), 2.46 (m, 3 H, P(CHMe₂)₃), 1.64 (d, 15 H, J_{PH} = 0.8 Hz, C₅Me₅), 1.23 (d, 12 H, ³J_{HH} = 7 Hz, CHMe₂), 1.21 (d, 6 H, ³J_{HH} = 7 Hz, CHMe₂), 1.16 (vq, 9 H, P(CHMeMe)₃), 1.03 (vq, 9 H, P(CHMeMe)₃), -15.07 (d, 1 H, ²J_{PH} = 29.4 Hz, OsH). ¹³C{¹H} NMR: 155.6, 148.5, 134.4, 119.7 (Ar), 94.1 (d, C₅Me₅), ²J_{PC} = 2.5 Hz), 34.19, 32.98, (CHMe₂) 28.32 (d, ¹J_{C-P} = 23.5 Hz, P(CHMe₂)₃), 24.90, 24.39, 23.79, 23.70, 19.73, 19.50 (CHMe₂), 10.29 (C₅Me₅). ²⁹Si NMR (CD₂Cl₂, δ): -53.0. ³¹P{¹H}

NMR (CD₂Cl₂, δ): 4.0. Anal. Calcd for C₃₄H₆₂BrOsPSi: C, 51.04; H, 7.81. Found: C, 51.17; H, 7.70.

Cp*(Pr₃P)Os(H)(Br)SiH₂(C₆F₅) (8). To a stirred solution of **2** (253 mg, 0.440 mmol) in CH₂Cl₂ (10 mL) was added 100 mg (0.505 mmol) of (C₆F₅)SiH₃ in CH₂Cl₂ (approximately 5 mL) by cannula, causing a rapid color change from purple to yellow-orange. The volume of the solution was reduced by half, and the flask was slowly cooled to -80 °C. After 24 h, well-formed orange crystals of **8** had formed. These crystals were isolated by filtration. Yield: 260 mg (77%). ¹H NMR (CD₂Cl₂, δ): 5.48 (dd, 1 H, J = 5 Hz, ¹J_{SiH} = 200 Hz), 3.98 (dd, 1 H, J = 5 Hz, ¹J_{SiH} = 201 Hz), 2.06 (m, 3 H, P(CHMe₂)₃), 1.71 (s, 15 H, C₅Me₅), 1.22–1.15 (2 overlapping vq, 18 H, P(CHMe₂)₃), -15.05 (d, 2 H, ²J_{PH} = 31.7 Hz, ²J_{SiH} = 5 Hz) Os(H)). ¹³C{¹H} NMR (CD₂Cl₂, δ): 95.1 (d, J_{PC} = 1 Hz, C₅Me₅), 27.9 (d, ¹J_{PC} = 26.0 Hz, P(CHMe₂)₃), 20.21, 19.95 (P(CHMe₂)₃), 10.42 (C₅Me₅). ¹⁹F{¹H} NMR (CD₂Cl₂, δ): -125.00 (m, *o*-C₆F₅), -155.85 (t, *p*-C₆F₅), -62.89 (m, *m*-C₆F₅). ²⁹Si{¹H} NMR (INEPT, CD₂Cl₂, δ): -62.2 (d, ²J_{PSi} = 13.5 Hz). ³¹P{¹H} NMR (CD₂Cl₂, δ): 6.68. Anal. Calcd for C₂₅H₃₉BrF₅OsPSi: C, 39.31; H 5.15. Found: C, 39.16; H, 5.20.

Cp*(Pr₃P)Os(H)(Br)SiH₂Hex (9). To a stirred solution of **2** (210 mg, 0.370 mmol) in C₅H₁₂ (10 mL) was added 52 mg (0.447 mmol) of HexSiH₃ in 20 mL of pentane. The solution immediately became a golden yellow. The volume of the solution was reduced to approximately 5 mL in vacuo, and the reaction vessel was slowly cooled to -80 °C. After 24 h at -80 °C, a fine, yellow, microcrystalline precipitate had formed. This product was isolated by filtration and dried in vacuo. Yield: 148 mg (58%). ¹H NMR (C₆D₆, δ): 5.38 (m, 1 H, ¹J_{SiH} = 183 Hz, OsSiHH), 4.39 (m, 1 H, ¹J_{SiH} = 167 Hz, OsSiHH), 2.48 (m, 3 H, P(CHMe₂)₃), 1.90 (m, 2 H, CH₂), 1.69–1.58 (m, overlapping, 2 H, CH₂), 1.42–1.36 (2 overlapping m, 4 H, CH₂), 1.38–1.35 (overlapping m, 1 H, Si(H)₂CHH), 1.18 (m, 1 H, Si(H)₂CHH), 1.09–1.02 (2 overlapping vq, P(CHMe₂)₃), 0.91 (t, ³J_{HH} = 7 Hz, CH₂CH₃), -15.36 (d, ²J_{PH} = 32.4 Hz, 1 H, OsH). ¹³C{¹H} NMR (C₆D₆, δ): 93.64 (d, J_{CP} = 1.8 Hz, C₅Me₅), 33.69, 32.36, 31.27 (CH₂), 28.01 (d, ¹J_{CP} = 26.8 Hz, P(CHMe₂)₃), 23.18 (CH₂), 20.36, 21.17, (P(CHMe₂)₃), 17.73 (SiH₂CH₂), 14.45, (CH₂Me), 10.44 (C₅Me₅). ³¹P{¹H} NMR (CD₂Cl₂, δ): 8.50. ²⁹Si{¹H} NMR (CD₂Cl₂, δ): -30.49 (d, ²J_{PSi} = 9 Hz). Anal. Calcd for C₂₅H₅₂BrOsPSi: C, 44.04; H, 7.69. Found: C, 44.17; H, 7.90.

Cp*(Pr₃P)Os(H)(Br)SiH₂Si(SiMe₃)₃ (10). To a solution of 479 mg of **2** (0.844 mmol) in Et₂O (15 mL) was added 239 mg (0.86 mmol) of (Me₃Si)₃SiSiH₃ in 20 mL of Et₂O by cannula, causing a rapid color change from purple to yellow and the precipitation of a microcrystalline solid. The heterogeneous mixture was stirred for an additional 5 min and then allowed to settle. The solid was collected by filtration and dried in vacuo. Yield: 581 mg (81%). ¹H NMR (C₆D₆, δ): 5.12 (s, 1 H, ¹J_{SiH} = 179 Hz, SiHH), 3.62 (s, 1 H, ¹J_{SiH} = 171 Hz, SiHH), 2.41 (m, 3 H, P(CHMe₂)₃), 1.62 (s, 15 H, C₅Me₅), 1.05 (vq, 9 H, P(CHMeMe)₃), 0.98 (vq, 9 H, P(CHMeMe)₃), 0.49 (s, 27 H, Si(SiMe₃)₃), -14.91 (d, 1 H ²J_{PH} = 30.8 Hz). ¹³C{¹H} NMR: 94.04 (C₅Me₅), 28.48 (d, ¹J_{CP} = 28.1 Hz, P(CHMe₂)₃), 20.48, 20.34, (P(CHMe₂)₃), 11.08 (C₅Me₅), 3.49 (Si(SiMe₃)₃). ²⁹Si NMR (gHMBC, C₆D₆, δ): -8.3 (SiH₂Si(SiMe₃)₃), -83.5 (d, ²J_{SiP} = 12 Hz, SiH₂Si(SiMe₃)₃), -134.0 (SiH₂Si(SiMe₃)₃). ³¹P{¹H} NMR (C₆D₆, δ): 8.81.

Cp*(Pr₃P)Os(H)(Br)SiH₂SiPh₃ (11). To a solution of 143 mg of **2** (0.252 mmol) in toluene (10 mL) was added 75 mg (0.253 mmol) of Ph₃SiSiH₃ in toluene (5 mL) by pipet, causing a rapid color change from purple to yellow. The mixture was concentrated in vacuo to a volume of approximately 10 mL, layered with pentane (15 mL), and cooled to -80 °C, affording a microcrystalline precipitate (60 mg), which was isolated by filtration and dried in vacuo. Solvent was removed in vacuo from the filtrate, affording an additional 60 mg of **11** as an analytically pure, fine yellow powder. Yield: 120 mg (55%). ¹H NMR (CD₂Cl₂, δ): 7.64 (m, 6 H, *o*-Ph), 7.32 (m, 9 H, *p*- and *m*-Ph), 4.84 (s, 1 H, ¹J_{SiH} = 178 Hz, SiHH), 3.19 (s, 1 H, ¹J_{SiH}

= 164 Hz, SiHH), 2.31 (m, 3 H, P(CHMe₂)₃), 1.59 (d, 15 H, $J_{\text{PH}} = 0.5$ Hz, C₅Me₅), 1.06 (vq, 9 H, P(CHMeMe)₃), 0.94 (vq, 9 H, P(CHMeMe)₃), -14.66 (d, 1 H, $^2J_{\text{PH}} = 31$ Hz, Os-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 138.9 (ipso-C), 136.4, 128.3, 127.4 (aryl), 94.53 (C₅Me₅), 28.73 (d, $^1J_{\text{CP}} = 26.7$ Hz, P(CHMe₂)₃), 19.82, 19.64 (P(CHMe₂)₃), 9.92 (C₅Me₅). ^{29}Si NMR (gHMBC, CD₂Cl₂, δ): -78.3 (d, $^2J_{\text{SiP}} = 9$ Hz, Os-SiH₂SiPh₃), -21.0 (Os-SiH₂SiPh₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 10.10. Anal. Calcd: C, 51.91; H, 6.36. Found: C, 52.63; H, 6.46.

Cp*(Pr₃P)Os(H)(Br)SiMe₂H (12). A solution of 113 mg (0.199 mmol) of **2** in Et₂O (15 mL) was degassed with a freeze-pump-thaw cycle. An atmosphere of Me₂SiH₂ was admitted to the reaction flask, causing the stirred solution to change immediately from a purple to a yellow color. The volatile components of the mixture were removed in vacuo to afford **12** as an analytically pure yellow-orange foam. Yield: 125 mg (92%). ^1H NMR (C₆D₆, δ): 6.16 (m, 1 H, $^1J_{\text{SiH}} = 178$ Hz, SiH) 2.41 (m, 3 H, P(CHMe₂)₃), 1.56 (d, 15 H, $J = 1$ Hz, C₅Me₅), 1.03 (vq, 9 H, P(CHMeMe)₃), 1.07 (vq, 9 H, P(CHMeMe)₃), 0.93 (d, 3 H, $^3J_{\text{HH}} = 4$ Hz, Si(H)MeMe), 0.91 (d, 3 H, $^3J_{\text{HH}} = 4$ Hz, Si(H)MeMe), -15.23 (d, 1 H, $^2J_{\text{PH}} = 31.9$ Hz, Os-H). ^1H NMR (CD₂Cl₂, δ): 5.50 (m, 1 H, $^1J_{\text{SiH}} = 178$ Hz, SiH), 2.48 (m, 3 H, P(CHMe₂)₃), 1.74 (d, 15 H, $J = 1$ Hz, C₅Me₅), 1.22-1.16, (2 overlapping vq, 18 H, P(CHMe₂)₃), 0.49 (d, 3 H, $^3J_{\text{HH}} = 4$ Hz, Si(H)MeMe), 0.39 (d, 3 H, $^3J_{\text{HH}} = 4$ Hz, Si(H)MeMe), -15.24 (d, 1 H, $^2J_{\text{PH}} = 31.7$ Hz, OsH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 94.06 (C₅Me₅), 28.16 (d, $^1J_{\text{PC}} = 26.5$ Hz), 20.74, 20.48 (P(CHMe₂)₃), 10.94 (C₅Me₅), 4.26, 0.94 (SiMe₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 5.66. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD₂Cl₂, HMBC, δ): -23.9. Anal. Calcd: C, 40.31, H 7.09. Found: C 40.44; H, 7.24

Cp*(Pr₃P)Os(H)(Br)SiPh₂H (13). To a stirred solution of 452 mg of **2** in pentane (40 mL) was added 157 mg (0.853 mmol) of Ph₂SiH₂ in pentane (5 mL) by cannula, causing a rapid color change from purple to yellow. The solution was filtered, concentrated to 2/3 its original volume, and cooled to -80 °C, affording a microcrystalline solid. Yield: 375 mg (78%). IR: ν_{SiH} 2080 cm⁻¹, ν_{OSiH} 2199 cm⁻¹. ^1H NMR (C₆D₆, δ): 8.11 (d, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, *o*-Ph), 8.07 (d, 2 H, $^3J_{\text{HH}} = 7.8$ Hz, *o*-Ph), 7.31-7.17 (m, overlapping, 9 H, aryl, SiH), 2.38 (m, 3 H, P(CHMe₂)₃), 1.47 (s, 15 H, C₅Me₅), 1.04 (vq, 9 H, P(CHMeMe)₃), 0.87 (vq, 9 H, P(CHMeMe)₃), -14.15 (d, 1 H, $^2J_{\text{PH}} = 32$ Hz, OsH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 145.7, 144.6, 137.4, 137.2, 127.4, 127.3, 127.0, 126.6 (aryl), 94.96 (C₅Me₅), 28.28 (d, $^1J_{\text{PC}} = 26.6$ Hz, P(CHMe₂)₃), 20.48, 20.33 (P(CHMe₂)₃), 10.76 (C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 3.79. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): -10.65 (d, $^2J_{\text{SiP}} = 9$ Hz). Anal. Calcd: C, 49.65; H, 6.45. Found: C, 49.47; H, 6.48.

[Cp*(Pr₃P)(H)₂Os=SiPh₂][B(C₆F₅)₄] (14). To a CD₂Cl₂ solution (1 mL) of **13** (25 mg, 33 μmol) was added 1.1 equiv of LiB(C₆F₅)₄ (26 mg, 38 μmol) in CD₂Cl₂ (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **14** to be the major (>95%) product in solution. ^1H NMR (CD₂Cl₂, δ): 7.86 (d, 4 H, *o*-Ph, $^3J_{\text{HH}} = 7$ Hz), 7.67 (t, 2 H, *p*-Ph, $^3J_{\text{HH}} = 8$ Hz), 7.61 (m, 4 H, *m*-Ph), 2.07 (s, 15 H, C₅Me₅), 1.88 (m, 3 H, P(CHMe₂)₃), 1.05 (vq, 18 H, P(CHMe₂)₃), -11.65 (d, 2 H, $^2J_{\text{PH}} = 28.4$ Hz, Os(H)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR: 143.0, 136.2, 133.8, 128.7 (aryl), 96.1 (C₅Me₅), 28.8 (d, $^1J_{\text{CP}} = 30$ Hz, P(CHMe₂)₃), 19.33 (P(CHMe₂)₃), 11.34 (C₅Me₅). ^{29}Si NMR (INEPT, CD₂Cl₂, δ): 313.6 (d, $^2J_{\text{SiP}} = 7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 39.6.

Cp*(Pr₃P)Os(H)₂SiPh₂OTf (15). To a stirred pentane solution of 324 mg (0.394 mmol) of **13** cooled in a CO₂/PrOH bath was added slowly an Et₂O (25 mL) solution of 114 mg (0.445 mmol) of AgOTf by cannula. The reaction vessel was protected from light and allowed to slowly come to room temperature. After 3 h, a dark, extremely fine precipitate had formed. The solution was filtered through a combination of Whatman #50 paper and glass fiber to afford an orange

solution. Volatile components of the mixture were removed in vacuo to afford a yellow-orange foam. NMR spectroscopy showed that the desired product was consistently contaminated with varying amounts (5-20%) of a second, unidentified species and unreacted starting material that was not removed by crystallization from pentane/Et₂O. Employing a molar excess of AgOTf (1.25 equiv) in the reaction did not increase the proportion of **15** in the product mixture. ^1H NMR (C₆D₆, δ): 8.17 (d, 4 H, $^3J_{\text{HH}} = 7$ Hz, *o*-aryl), 7.29 (m, 4 H, $^3J_{\text{HH}} = 7$ Hz, *m*-aryl), 7.16 (m, 2 H, *p*-aryl), 1.61 (m, 3 H, P(CHMe₂)₃), 1.59 (s, 15 H, C₅Me₅), 0.87 (vq, 18 H, P(CHMe₂)₃), -14.34 (d, 2 H, $^2J_{\text{PH}} = 28$ Hz, OsH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, δ): 30.0. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 64.1 (d, $^2J_{\text{PSi}} = 24.6$ Hz).

[Cp*(Pr₃P)(H)₂Os=SiH₂][B(C₆F₅)₄]_n (16). To a CD₂Cl₂ solution (1 mL) of **3** (20 mg, 33 μmol) was added 1.1 equiv of LiB(C₆F₅)₄ (25 mg, 36 μmol) in CD₂Cl₂ by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was filtered through a fine glass fiber, affording a clear yellow solution. ^1H NMR spectroscopy showed **16** to be the major (>95%) product in solution. NMR (^1H , CD₂Cl₂, δ): 6.2 (br s, LW = 500 Hz, fwhh), 1.79 (m, 3 H, P(CHMe₂)₃), 1.77 (s, 15 H, C₅Me₅), 0.87 (vq, 18 H, P(CHMe₂)₃), -14.77 (br s, LW = 100 Hz, fwhh, 2 H, OsH). $^{31}\text{P}\{^1\text{H}\}$ (CD₂Cl₂, δ): 32.5 (LW = 150 Hz, fwhh).

[Cp*(Pr₃P)(H)₂Os=Si(H)dipp][B(C₆F₅)₄] (17). To a CD₂Cl₂ solution (1 mL) of **6** (31 mg, 40 μmol) was added LiB(C₆F₅)₄ (30 mg, 44 μmol) in 0.75 mL of CD₂Cl₂ by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **17** to be the major (>95%) product in solution. ^1H NMR (CD₂Cl₂, δ): 11.61 (s, 1 H, $^1J_{\text{SiH}} = 188$ Hz OsSi(H)), 7.35 (t, 1 H, $^3J_{\text{HH}} = 8$ Hz, *p*-aryl), 7.26 (d, 2 H, $^3J_{\text{HH}} = 8$ Hz, *m*-aryl), 2.73 (sept, 2 H, $^3J_{\text{HH}} = 6.4$ Hz, *m*-CHMe₂), 2.07 (m, 3H, P(CHMe₂)₃), 2.04 (s, 15 H, C₅Me₅), 1.34 (d, 12 H, $^3J_{\text{HH}} = 6.4$ Hz, *m*-CHMe₂), 1.14 (vq, 18 H, P(CHMe₂)₃), -12.72 (d, 2 H, $^2J_{\text{PH}} = 27.9$ Hz, Os-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 151.2, 136.5, 133.1 123.3 (aryl), 97.4 (C₅Me₅), 37.4 (*m*-CHMe₂), 28.3 (d, $^1J_{\text{CP}} = 29$ Hz, P(CHMe₂)₃), 24.1 (*m*-CHMe₂), 18.6 (P(CHMe₂)₃), 10.89 (C₅Me₅). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 314 (d, $^2J_{\text{SiP}} = 15$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 32.4.

[Cp*(Pr₃P)(H)₂Os=Si(H)trip][B(C₆F₅)₄] (18). To a solution of 310 mg (0.387 mmol) of **7** in 10 mL of fluorobenzene was added a solution of 275 mg (0.401 mmol) of Li[B(C₆F₅)₄] in 10 mL of fluorobenzene. The solution immediately turned from golden yellow-orange to pale lemon yellow. A fine white precipitate formed at the same time. The mixture was filtered and the volatile material was removed in vacuo to afford a pale yellow foam, which was then dried in vacuo. Yield: 373 mg (73%). ^1H NMR (CD₂Cl₂, δ): 11.56 (s, 1 H, $^1J_{\text{SiH}} = 183$ Hz, Os=Si(H)trip), 7.06 (s, 2 H, Ar), 2.92 (sept, 1 H, $^3J_{\text{HH}} = 7$ Hz, CHMe₂), 2.72 (sept, 2 H, $^3J_{\text{HH}} = 7$ Hz, CHMe₂), 2.0-2.1 (m, 3 H, P(CHMe₂)₃), 2.04 (s, 15 H, C₅Me₅), 1.34 (d, 12 H, $^3J_{\text{HH}} = 7$ Hz, CHMe₂), 1.25 (d, 6 H, $^3J_{\text{HH}} = 7$ Hz, CHMe₂), 1.13 (vq, 18 H, P(CHMe₂)₃), -12.74 (d, 2 H, $^2J_{\text{PH}} = 27$ Hz, $^2J_{\text{SiH}} = 5.5$ Hz Os-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 155.3, 151.8, 134.2, 121.9 (Ar), 97.81 (d, C₅Me₅, $^2J_{\text{PC}} = 2.5$ Hz), 37.86, 35.06 (CHMe₂), 28.79 (d, $^1J_{\text{CP}} = 30.0$ Hz, P(CHMe₂)₃), 24.57, 23.94, 19.08 (CHMe₂), 11.31 (C₅Me₅). ^{29}Si (HMBC expt, CD₂Cl₂, δ): 315 (dd, $^2J_{\text{SiP}} = 13.6$ Hz, $^2J_{\text{SiH}} = 5.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, δ): 32.5. Anal. Calcd for C₅₈H₆₂BF₂₀OSi: C, 49.79; H, 4.47. Found: C, 50.04; H, 4.31.

[Cp*(Pr₃P)(H)₂Os=Si(H)Si(SiMe₃)₃][B(C₆F₅)₄] (19). To a CD₂Cl₂ solution (0.75 mL) of **10** (28 mg, 33 μmol) was added LiB(C₆F₅)₄ (25 mg, 36 μmol) in CD₂Cl₂ (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a

fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **19** to be the major (>95%) product in solution. ^1H NMR (CD_2Cl_2 , δ): 12.05 (t, 1 H, $^2J_{\text{HH}} = 2.5$ Hz, $^1J_{\text{SiH}} = 147.6$ Hz, OsSiH), 2.18 (s, 15 H, C_5Me_5), 1.76 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 1.22 (vq, 18 H, $\text{P}(\text{CHMe}_2)_3$), 0.40 (s, $^2J_{\text{SiH}} = 5.9$ Hz, 27 H, Si(SiMe_3)₃), -9.90 (d, $^2J_{\text{PH}} = 27.5$ Hz, OsH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 96.43 (C_5Me_5), 31.07 (d, $^1J_{\text{PH}} = 29$ Hz, $\text{P}(\text{CHMe}_2)_3$), 19.45 ($\text{P}(\text{CHMe}_2)_3$), 12.17 (C_5Me_5), 3.20 (SiMe_3). ^{29}Si NMR (HMBC): 417.5 (d, $^2J_{\text{PSi}} = 9$ Hz, OsSi(H)Si(SiMe_3)₃), -5.9 (OsSi(H)Si(SiMe_3)₃), -74.9 (OsSi(H)Si(SiMe_3)₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): 40.88.

[Cp* $\{\text{Pr}_3\text{P}(\text{H})_2\text{Os}=\text{Si}(\text{H})(\text{C}_6\text{F}_5)_4\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (20). To a CD_2Cl_2 solution (0.75 mL) of **8** (22 mg, 29 μmol) was added $\text{LiB}(\text{C}_6\text{F}_5)_4$ (22 mg, 32 μmol) in CD_2Cl_2 (0.75 mL) by pipet, causing a color change from golden yellow to lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **20** to be the major (>95%) product in solution. ^1H NMR (CD_2Cl_2 , δ): 6.75 (br s, 1 H, $^1J_{\text{SiH}} = 185$ Hz), 1.92–2.20 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 2.05 (s, 15 H, C_5Me_5), 1.08–1.18 (vq, 18 H, $\text{P}(\text{CHMe}_2)_3$), -14.09 (d, $^2J_{\text{PH}} = 27.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: 95.50 (C_5Me_5), 28.95 (d, $^1J_{\text{PC}} = 27.7$ Hz, $\text{P}(\text{CHMe}_2)_3$), 18.92 ($\text{P}(\text{CHMe}_2)_3$), 11.20 (C_5Me_5). $^{19}\text{F}\{^1\text{H}\}$ NMR: -128.8 (br, $o\text{-C}_6\text{F}_5$), -150.9, 160.8, (C_6F_5). ^{29}Si NMR (HMBC expt, CD_2Cl_2 , δ): 318 br. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 29.9.

[Cp* $\{\text{Pr}_3\text{P}(\text{H})_2\text{Os}=\text{Si}(\text{H})\text{SiPh}_3\text{DMAP}[\text{B}(\text{C}_6\text{F}_5)_4]$ (21·DMAP). To a CD_2Cl_2 solution (1 mL) of **11** (19 mg, 22 μmol) and DMAP (3 mg, 25 μmol) was added a CD_2Cl_2 solution (0.75 mL) of $\text{LiB}(\text{C}_6\text{F}_5)_4$ (17 mg, 25 μmol) by pipet, causing a color change from golden yellow to very pale yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and was then filtered through a fine glass fiber, affording a clear yellow solution. NMR spectroscopy showed **21·DMAP** to be the major (>95%) product in solution with excess DMAP. ^1H NMR (CD_2Cl_2 , δ): 7.81 (d, 2 H, $^3J_{\text{HH}} = 7.5$ Hz, DMAP), 7.46 (m, 6 H, aryl), 7.40 (m, 3 H, aryl), 7.32 (m, 6 H, aryl), 6.47 (d, 1 H, $J = 2.5$ Hz, $^1J_{\text{SiH}} = 169$ Hz, Si-H), 6.35 (d, 2 H, $^3J_{\text{HH}} = 7.5$ Hz, DMAP), 3.10 (s, 6 H, NMe_2), 2.09 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 1.84 (s, 15 H, C_5Me_5), 1.02 (vq, 9 H, $\text{P}(\text{CHMe}_2)_3$), 0.93 (vq, 9 H, $\text{P}(\text{CHMe}_2)_3$), -14.65 (d, 1 H, $^2J_{\text{PH}} = 29$ Hz, Os-H), -14.71 (d, 1 H, $^2J_{\text{PH}} = 28$ Hz, Os-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 145.8 (DMAP aryl), 136.4, 136.3, 129.7, 128.4 (aryl), 106.8 (DMAP aryl), 94.4 (C_5Me_5), 39.9 (NMe_2), 26.8 (d, $^1J_{\text{PC}} = 29.7$ Hz, $\text{P}(\text{CHMe}_2)_3$), 18.8 ($\text{P}(\text{CHMe}_2)_3$), 11.62 (C_5Me_5).

[Cp* $\{\text{Pr}_3\text{P}(\text{H})_2\text{Os}=\text{Si}(\text{Ph})\text{SiPh}_2\text{H}[\text{B}(\text{C}_6\text{F}_5)_4]$ (22). To a CD_2Cl_2 solution (1 mL) of **11** (26 mg, 30 μmol), a CD_2Cl_2 solution (0.75 mL) of $\text{LiB}(\text{C}_6\text{F}_5)_4$ (23 mg, 34 μmol) was added by pipet, causing a color change from golden yellow to pale lemon yellow and the formation of a fine white precipitate. The mixture was allowed to stand for 30 min and filtered through a fine glass fiber. NMR spectroscopy showed **22** to be the major (>95%) product in solution. ^1H NMR (CD_2Cl_2 , δ): 8.24 (d, 2 H, $o\text{-PH}$, $^3J_{\text{HH}} = 8$ Hz), 7.72–7.44 (overlapping m, 13 H, aryl), 5.79 (s, 1 H, $^1J_{\text{SiH}} = 198$ Hz, $^2J_{\text{SiH}} = 7$ Hz, SiH), 1.99 (s, 15 H, C_5Me_5), 1.70 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 0.94 (vq, 18 H, $\text{P}(\text{CHMe}_2)_3$), -10.58 (d, 2 H, $^2J_{\text{PH}} = 28.2$ Hz, $^2J_{\text{SiH}} = 13.5$ Hz, Os-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 136.3, 135.9, 135.7, 134.0, 130.4, 129.8, 128.8, 128.5 (aryl), 95.7 (d, $J_{\text{PC}} = 1$ Hz, C_5Me_5), 28.5 (d, $^1J_{\text{PC}} = 29.8$ Hz, $\text{P}(\text{CHMe}_2)_3$), 18.8 ($\text{P}(\text{CHMe}_2)_3$), 11.0 (C_5Me_5). ^{29}Si NMR (HMBC, CD_2Cl_2 , δ): 379, -18. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 41.4.

{Cp* $\{\text{Pr}_2\text{P}(\eta^2\text{-MeC}=\text{CH}_2)\text{OsH}_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (24). Solid **2** (545 mg, 0.94 mmol) and solid $\text{KB}(\text{C}_6\text{F}_5)_4$ (750 mg, 1.04 mmol) were combined in a Schlenk tube and cooled to -78°C with a dry ice/ PrOH bath. THF (10 mL) was added, and the mixture was stirred for 5 min at -78°C and then allowed to come to room temperature. After 1 h at room temperature, solvent was removed in vacuo. The dark residue was extracted with 3×10 mL of 1:1 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. The combined filtrates were cooled

slowly to -80°C , affording a crop of well-formed taupe crystals. Yield: 540 mg (46%). ^1H NMR (CD_2Cl_2 , δ): 3.12 (d, 1 H, $J_{\text{PH}} = 35$ Hz, $\text{MeC}=\text{CHH}$), 2.54 (d, 3 H, $J_{\text{PH}} = 8$ Hz, $\text{MeC}=\text{CHH}$), 2.37 (m, 1 H, $\text{P}(\text{CHMe}_2)_3$), 2.24 (s, 15 H, C_5Me_5), 2.24 (d, overlapping, 1 H, $J_{\text{PH}} = 12$ Hz, $\text{MeC}=\text{CHH}$), 1.60–1.53 (3 overlapping vq, 9 H, $\text{P}(\text{CHMe}_2)_3$), 1.55–1.52 (m, overlapping, 1 H, $\text{P}(\text{CHMe}_2)_3$), 1.41 (vq, 3 H, $\text{P}(\text{CHMe}_2)_3$), -13.74 (d, 1 H, OsH, $^2J_{\text{PH}} = 23.1$ Hz), -15.10 (d, 1 H, OsH, $^2J_{\text{PH}} = 20.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 98.28 (C_5Me_5), 57.79 (d, $^2J_{\text{PH}} = 20.3$ Hz, $\text{MeC}=\text{CH}_2$), 33.42 (d, $^2J_{\text{PH}} = 37.5$ Hz, $\text{P}(\text{CHMe}_2)_3$), 32.70 (s, $\text{MeC}=\text{CH}_2$), 26.55 (s, $\text{MeC}=\text{CH}_2$), 24.92, 22.55 (s, $\text{P}(\text{CHMe}_2)_3$), 22.08 (d, $^2J_{\text{PH}} = 22.3$ Hz, $\text{P}(\text{CHMe}_2)_3$), 19.81, 18.73 (s, $\text{P}(\text{CHMe}_2)_3$), 11.73 (s, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): -4.62. Anal. Calcd: C, 44.34; H, 3.12. Found: C, 44.06; H, 3.29.

Cp* $\{\text{Pr}_2\text{P}(\eta^2\text{-MeC}=\text{CH}_2)\text{OsH}$ (25). A 468 mg (0.377 mmol) sample of **9** was treated with 10 mL of C_6H_6 , affording a dense, mobile oil at the bottom of the vessel. The mixture was stirred, forming a heterogeneous suspension. This suspension was treated with $\text{KN}(\text{SiMe}_3)_2$ (80 mg, 0.40 mmol) in C_6H_6 (30 mL). The solution rapidly became homogeneous as the cationic species reacted, and a white precipitate, presumably $\text{KB}(\text{C}_6\text{F}_5)_4$, formed. The solution was allowed to settle and was filtered to afford a pale yellow solution. Removal of solvent from the filtrate afforded a dense, gelatinous oil that did not solidify upon prolonged exposure to vacuum or treatment with pentane. Attempts to isolate this compound as a solid suitable for elemental analysis were unsuccessful. NMR tube reactions and spectroscopy of the viscous oil both demonstrated that **25** is formed in greater than 95% yield from **24** in C_6D_6 . ^1H NMR (C_6D_6 , δ): 2.27 (m, 1 H, $\text{MeC}=\text{CHH}$), 2.05 (s, 15 H, C_5Me_5), 1.98 (m, 1 H, $\text{MeC}=\text{CHH}$), 1.71 (m, 1 H, $\text{P}(\text{CHMe}_2)_3$), 1.56 (m, 3 H, $\text{P}(\text{CHMe}_2)_3$), 1.52 (d, 3 H, $^3J_{\text{PH}} = 6$ Hz, $\text{MeC}=\text{CHH}$), 1.19 (vq, 3 H, $\text{P}(\text{CHMe}_2)_3$), 1.11 (vq, 1 H, $\text{P}(\text{CHMe}_2)_3$), 0.91–0.85 (2 overlapping vq, 6 H, $\text{P}(\text{CHMe}_2)_3$), -16.18 (dd, 1 H, $J_{\text{HH}} = 8$ Hz, $^2J_{\text{PH}} = 26$ Hz, OsH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 88.11 (d, $J_{\text{PH}} = 0.8$ Hz, C_5Me_5), 27.08 (d, $^1J_{\text{PH}} = 31$ Hz, $\text{P}(\text{CHMe}_2)_3$), 23.10 (d, $^2J_{\text{PH}} = 6.7$ Hz, $\text{P}(\text{CHMe}_2)_3$), 20.84 (d, $^2J_{\text{PH}} = 21$ Hz, $\text{MeC}=\text{CH}_2$), 20.62 (d, $^2J_{\text{PH}} = 4$ Hz, $\text{P}(\text{CHMe}_2)_3$), 20.39 (d, $^2J_{\text{PH}} = 6.7$ Hz, $\text{P}(\text{CHMe}_2)_3$), 19.84 (d, $^2J_{\text{PH}} = 2.4$ Hz, $\text{P}(\text{CHMe}_2)_3$), 18.88 (d, $^2J_{\text{PH}} = 4.5$ Hz, $\text{P}(\text{CHMe}_2)_3$), 16.95 (d, $^3J_{\text{PH}} = 21.2$ Hz, $\text{P}(\text{CHMe}_2)_3$), 12.30 (C_5Me_5), 12.15 (d, $^2J_{\text{PH}} = 15$ Hz, $\text{MeC}=\text{CH}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 4.82.

X-ray Crystallography. General Considerations. Crystallographic analyses were carried out at the University of California, Berkeley CHEXRAY crystallographic facility.³⁹ All measurements were made on a Bruker SMART CCD area detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Crystals were mounted on capillaries with Paratone-N hydrocarbon oil and held in a low-temperature N_2 stream during data collection. Frames were collected using ω scans at 0.3° increments, using exposures of 10 s (**4**, **8**, **11**, **15**, and **24**) or 20 s (**12** and **13**). Data were integrated with the program SAINT,⁴⁰ corrected for Lorentz and polarization effects, and analyzed for agreement and possible absorption using XPREP.⁴¹ Empirical absorption corrections were made with either SADABS⁴² or XPREP. A p -factor of 0.030 was employed to downweight intense reflections. Structures were solved by direct methods and expanded using Fourier techniques.⁴³ The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were

(39) <http://xray.cchem.berkeley.edu>.

(40) SAINT: SAX Area-Detector Integration Program, version 4.024; Bruker, Inc.: Madison, WI, 1995.

(41) XPREP v. 5.03, Part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(42) Sheldrick, G. M. SADABS, Siemens Area Detector Absorption Correction Program; 1996. Advance copy, private communication.

Table 3. Experimental Details for X-ray Crystallography

	4	8	11·C ₆ H ₆	12·(C ₆ H ₅ F) _{0.5}
empirical formula	C ₂₅ H ₄₄ BrOsSiP	C ₂₅ H ₃₉ F ₅ SiPOsBr	C ₄₃ H ₆₀ OsPSi ₂ Br	C ₂₄ H ₄₃ OsSiBrPF _{0.50}
fw	673.79	763.74	934.20	670.27
cryst color and habit	yellow blade	orange shard	yellow plate	yellow block
cryst size (mm)	0.29 × 0.1 × 0.02	0.20 × 0.09 × 0.05	0.15 × 0.10 × 0.07	0.11 × 0.09 × 0.07
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice type	primitive	primitive	C-centered	primitive
space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>Cc</i> (#9)	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>a</i> (Å)	9.242(1)	15.5293(1)	9.364(2)	9.0114(1)
<i>b</i> (Å)	17.895(2)	9.1041(1)	28.9855(5)	20.7564(9)
<i>c</i> (Å)	16.121(2)	19.8726(3)	15.5909(3)	14.876(3)
α (deg)	90	90	90	90
β (deg)	95.507	99.319(1)	104.671(1)	91.25(1)
γ (deg)	90	90	90	90
volume (Å ³)	2653.9(4)	2772.51(5)	4093.7(5)	2781.9(3)
orientation refln, 2θ range (deg)	3.4–51.3	3.4–50.9	3.4–51.2	3.4–51.2
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (g/cm ³)	1.69	1.830	1.516	1.600
<i>F</i> ₀₀₀	1336	1496	1888	1326
μ(Mo Kα) (cm ⁻¹)	64.38	61.89	42.18	61.39
temperature (°C)	–112	–109	–119	–105
data collected, 2θ _{max} (deg)	51.3	50.9	51.1	50.9
no. of reflns measd, total	11 889	12 218	10 796	5495
no. of reflns measd, unique	4531	4874	5115	4074
<i>R</i> _{int}	0.057	0.036	0.035	.034
transmn factors, <i>T</i> _{min} / <i>T</i> _{max}	0.15/0.88	0.41/0.65	0.50/0.72	0.50/0.61
no. of obsd data <i>I</i> > 3σ	2911	3608	4540	2925
no. of params refined	262	307	431	242
refln/param ratio	11.11	11.75	10.53	12.09
final residuals <i>R</i> ; <i>R</i> _w ; <i>R</i> _{all} ^a	0.042, 0.049, 0.065	0.034; 0.041; 0.044	0.038; 0.044; 0.043	0.064; 0.096; 0.078
goodness of fit indicator ^b	1.20	1.34	1.51	3.16
max. shift/error in final LS cycle	0.01	0.00	0.01	0.03
max.; min. peaks (e ⁻ /Å ³)	2.91; –3.78	1.35; –2.63	1.72; –2.31	2.64; 4.46
	13·(C ₅ H ₁₂) ₂	15	24	
empirical formula	Os ₂ Si ₂ P ₂ Br ₂ C ₇₄ H ₁₀₀	OsPC _{35.5} F ₃ SSiO ₃ H ₄₈ Br _{0.05}	C ₄₃ F ₂₄ POsH ₃₆ B	
fw	1647.93	865.08	1240.70	
cryst color and habit	yellow plate	yellow prism	amber block	
cryst size (mm)	0.19 × 0.17 × 0.07	0.26 × 0.23 × 0.16	0.13 × 0.11 × 0.08	
cryst syst	monoclinic	triclinic	monoclinic	
lattice type	primitive	primitive	primitive	
space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 1 (#2)	<i>P</i> 2 ₁ / <i>c</i> (#14)	
<i>a</i> (Å)	13.5150(3)	9.1510(2)	17.1214(6)	
<i>b</i> (Å)	39.3983(9)	11.9720(3)	14.1558(6)	
<i>c</i> (Å)	14.3453(3)	18.1370(1)	19.3014(6)	
α (deg)	90	81.930(1)	90	
β (deg)	98.738(1)	77.270(1)	114.089(1)	
γ (deg)	90	76.040(1)	90	
volume (Å ³)	7549.8(3)	1872.92(6)	4270.6(2)	
orientation reflns, 2θ range (deg)	3.4–51.4	3.5–45.0	3.4–49.4	
<i>Z</i>	4	2	4	
<i>D</i> _{calc} (g/cm ³)	1.450	1.534	1.930	
<i>F</i> ₀₀₀	3296	869.5	2424	
μ(Mo Kα) (cm ⁻¹)	45.28	36.33	31.61	
temperature (°C)	–113	–127	–132	
data collected, 2θ _{max} (deg)	51.5	50.8	49.4	
no. of reflns measd, total	39 351	9183	18 809	
no. of reflns measd, unique	13 103	5884	7343	
<i>R</i> _{int}	0.058	0.036	0.055	
transmn factors, <i>T</i> _{min} / <i>T</i> _{max}	0.43/0.67	0.20/0.59	0.52/0.78	
no. of obsd data <i>I</i> > 3σ	8826	4986	4487	
no. of params refined	723	400	475	
refln/param ratio	12.21	12.46	9.45	
final residuals <i>R</i> ; <i>R</i> _w ; <i>R</i> _{all} ^a	0.037; 0.045; 0.064	0.038; 0.046; 0.042	0.034; 0.038; 0.065	
goodness of fit indicator ^b	1.17	1.43	1.06	
max. shift/error in final LS cycle	0.04	0.02	0.03	
max.; min. peaks (e ⁻ /Å ³)	2.74; 1.92	1.86; –2.78	0.92; –1.66	

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. ^b GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

corrected for both the real and the imaginary components of anomalous dispersion. Calculations were performed using the teXsan crystallographic software package.⁴⁴ In each case, the calculated centroid of the Cp* ring was placed in a fixed position as a carbon atom with a partial occupancy of 0.0001 and a fixed *B*_{iso} of 0.2 and included in the final cycles of least-squares refinement. Osmium hydride ligands could not be

reliably located in the Fourier difference maps and were not included in the refinement. Unless stated otherwise, non-hydrogen atoms were allowed to refine anisotropically, and carbon-bound hydrogen atoms were placed at calculated positions and not refined.

Selected experimental parameters for data collection and refinement are presented above in Table 3. Atomic coordinates,

anisotropic thermal parameters, and selected bond lengths and angles are collected in the Supporting Information.

For 4. Crystals were grown by slow diffusion of pentane into a benzene solution. The relatively large residual peaks in the Fourier density map are a symptom of an imperfect absorption correction due to the bladeliike morphology of the crystals. The largest peaks in the Fourier map are symmetrically disposed about osmium.

For 8. Crystals were grown by slow cooling of a concentrated $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution. The structure is of high quality, and no problems were encountered in the refinement. The largest peaks in the Fourier map were located close to osmium.

For 11. Crystals were grown by layering a concentrated C_6D_6 solution with pentane. There is one well-ordered molecule of benzene per molecule of **11**. The structure is of high quality, and no problems were encountered in the refinement. The correct choice of enantiomorph was verified by refinement to a low R value and a successful Bijvoet analysis. The largest peaks in the Fourier map were located close to osmium.

For 12. Crystals were grown from a concentrated fluorobenzene/pentane solution at $-30\text{ }^\circ\text{C}$. After collection of the data set, careful inspection of the data showed that the crystal had fractured in the cold stream midway through collection. Data collected after this event were discarded, significantly reducing the redundancy of the data (total/unique data = 1.34). Despite this difficulty, the model refined to an acceptable R value, and bond lengths and angles were reasonable. The asymmetric unit contains half of a molecule of fluorobenzene located on an inversion center. This solvent molecule was refined isotropically. The largest peaks in the Fourier map were located close to osmium.

For 13. Crystals were grown by layering a concentrated C_6D_6 solution with pentane. The asymmetric unit contains two crystallographically independent molecules of **13** which have essentially identical metric parameters. The unit cell has

sizable channel-shaped voids that are filled with disordered pentane. This disordered solvent was successfully modeled as a series of half-occupancy carbon atoms. The largest peaks in the Fourier map were located close to osmium.

For 15. Crystals were grown by layering a toluene solution containing **15** as the major constituent with pentane. The asymmetric unit contains half of a molecule of toluene on an inversion center. A large peak close to osmium was at the appropriate distance for an osmium-bound bromine atom and was modeled as such at 5% occupancy. The partial occupancy of bromine at this location can be attributed to cocrystallization of a small amount of the precursor material **13**. Other large peaks in the Fourier map were located close to osmium.

For 24. Crystals were grown by slow cooling of a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution. The 24 carbon atoms of the $\text{B}(\text{C}_6\text{F}_5)_4$ anion were allowed to refine isotropically to maintain a high data/parameter ratio. A model in which these carbons were refined anisotropically did not provide significantly different metric parameters. Hydrogen atoms bound to the sp^2 carbon atom in the metalated P^iPr_3 ligand were located in the Fourier map and fixed in the final stages of refinement. The largest residual peaks in the Fourier difference map were close to osmium.

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Supporting Information Available: Tables of atomic coordinates, thermal displacement parameters, and selected bond lengths and angles for **4**, **8**, **11**, **12**, **13**, **15**, and **24**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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